DETERMINATION AND CHARACTERISATION OF TRACE METALS AND PERSISTENT ORGANIC POLLUTANTS IN BAYNESPRUIT RIVER, SOBANTU, KWAZULU-NATAL, SOUTH AFRICA.

by

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I declare that the above dissertation/thesis is my own work and that all the sources that I have used or quoted have been indicated and acknowledged by means of complete references.

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SIGNATURE DATE

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I dedicate this work to my loving wife Samke Zuma and my boys; Mnqobi and Ntandoyenkosi Zuma.

ABSTRACT

This study assesses the presence of selected trace metals and pops in the Baynespruit River, Sobantu, KwaZulu-Natal. Sediments, plants and water samples were collected along the river during dry and wet season. For metal analysis, the extraction was done using acid digestion and then determined on the inductively coupled plasma atomic emission spectroscopy, for total metals in sediments, plants and water. Bio-available metals in sediments were analysed using atomic absorption spectroscopy. POPs were extracted in sediments using soxhlet extraction, which was followed up by evaporation on the rotary evaporator, sample clean up on a GPC column, further sample concentration on the rotary evaporator and later analysed on GC/MS instrument. Metals of concern in both seasons were Cu, Cr, Pb and Zn which exceeded maximum permissible limits for South African soil, Cr was just about the maximum permissible limit. The targeted POPs were not detected on any site during this work.

Key terms: sediments, metals, plant metals, metals in water, POPs, metal concentration, analytical, extraction, analysis.

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ACRONYMS AND ABBREVIATIONS:

Ambic	Ammonium bicarbonate
Cl	Chlorides
DWAF	Department of water affairs and forestry
EC	Electrical Conductivity
FAO	Food and Agriculture Organization of the United Nations
GC/MS	Gas Chromatography Mass Spectroscopy
GPS	Global Positioning System
ICP-OES	Inductively Coupled Plasma Optical Emission Spectroscopy
KCl	Potassium chloride
KZN DARD	KwaZulu-Natal Department of Agriculture and Rural development
LoD	Limit of Detection
Na_2EDTA	Disodium ethylenediaminetetraacetate dihydrate
POPs	Persistent organic pollutants
r.p.m	Rotation per minutes
TDS	Total Dissolved Solids
Tot. Alkalinity	Total alkalinity
USEPA	United State Environmental Protection Agency
WHO	World Health Organisation

CHAPTER ONE: INTRODUCTION

1.1 Background Information

Metals and persistent organic pollutants (POPs) are important pollutants of aquatic environments (Florescu *et al.,* 2011; Dennis *et al.,* 2013). In fact pollution of water by these chemical agents has become a global problem (Ademola *et al.*, 2014). Aquatic environments include systems such as lakes, oceans and rivers. The introduction of these pollutants in the aquatic systems presents a toxicity problem for the environment, and threatens human health (Craffod and Avenant-Oldewase, 2010).

Chemicals enter aquatic systems from point and non-point sources. Point sources are pollution source associated with a point location of a pollutant. An example of a point source is a chemical spill. Point sources of pollution are easy to track and to quantify. On the other hand, non-point sources are associated with diffuse and wide source of pollution. An example of non-point source of pollution is the flow or agrochemical from fields into water streams. Non-point sources are difficult to trace and to quantify (Jackson *et al*., 2013).

1.2 Metals overview

Metals are present in the environment in different amounts and they have different functions. These metals may be toxic by nature, for example, cadmium, or they may become toxic at high concentration, for example magnesium. Some metals such as magnesium, calcium, iron, zinc, manganese, boron, sodium, and potassium are required by living organisms in small quantities; once they increase above the required level they become toxic (Su *et al*., 2014; Mahakalkar *et al.,* 2013). Some of the trace metals known to be a problem in aquatic systems include, chromium (Cr), zinc (Zn), nickel (Ni), copper (Cu), arsenic (As), aluminium (Al), lead (Pb), vanadium (V), magnesium (Mg), titanium (Ti) (Doong *et al.,* 2008, Sukdeo *et al.,* 2012).

Metals are non-biodegradable; this means once they are mobilized they accumulate in the environment. They remain in the water, sediments or biota if they became ingested or absorbed. This means, even small quantities of trace metals pose a threat since they can bio-accumulate or increase by bio-magnification (Dennis *et al.,* 2013; Mahakalkar *et al.,* 2013). Bio-magnification is a process whereby pollutants increase up the food chain from the source of pollution (Pellacani *et al*., 2012; Kang *et al*., 2013). The bioaccumulation of trace metals is what makes them to be dangerous

since their concentration in dynamic waters can be very low, sometimes, below detection level (Adeniyi *et al.,* 2011). For example, a fish can take in water contaminated with low levels of mercury. The mercury will remain inside the fish and increase every time the fish takes in the water. The fish is linked into the human food chain, by the time the mercury reaches the human it will be concentrated enough to be toxic (Opaluwa *et al.,* 2012).

Metals occur naturally from weathering of rocks and soil (Mmualefe and Torto, 2011; Sparks *et al*., 2017). However, human activities have tremendously increased the levels of these metals in the environment. In fact, it is estimated that the human induced inputs of metals such as arsenic, nickel, and zinc in the environment is often more than double the natural inputs (Sukdeo *et al.,* 2012). The major human activities which results in mobilization of metals include domestic waste water effluents (especially As, Cr, Cu, Mn and Ni), coal burning power plants (As, Hg, & Se in particular), iron and steel plants (Cr, Mo, Sb and Zn) and dumping of sewage sludge (As, Mn, Pb) (Craffod and Avenant-Oldewase, 2010).

Soil pollution is another source of metal pollution in rivers (Florescu *et al.,* 2011; Razanica *et al.,* 2014). Soil polluted by industrial chemicals, waste dumps, and accidental spillages provide a medium for these pollutants to reach aquatic systems by surface runoff (Dennis *et al.,* 2013). Agriculture chemicals applied to crops and on soil contribute to pollution as well. Pesticides have been shown to be responsible for large fish kills in certain parts of South Africa (Roux *et al*., 1994; Dennis *et al.,* 2013).

Once metals have been mobilized and enter the aquatic system they follow various ways of transportation. Since the water column is dynamic, it usually has low concentration of trace metals (Adeniyi *et al.,* 2011). Some of the biota, such as fish in the water ingest these trace metals (Crafford and Avenant-Oldewage, 2010). Once in the organism trace metals then either bio-concentrate as the organism keeps on ingesting contaminated water (Opaluwa *et al.,* 2012; Mahakalkar *et al.,* 2013) or bio-accumulate as secondary feeders feed on it. Some of these contaminants find way to the sediments where they bind on particles. Because of this binding, sediments provide a region of high concentrated metals in aquatic systems (Baran *et al.,* 2015). In fact, above 90 % of metals in aquatic environment is associated with particulate matter especially the fine particles, in turn the sediments releases these metals back

into the water column slowly overtime presenting more pollution complications in terms of trace metal clean up (Tirkey *et al.,* 2012).

1.3 POPs overview

Persistent Organic Pollutants are toxic chemical substances introduced in the environment by anthropogenic activities and are able to bio concentrate through the food web (Nash, 2011). There is a wide spectrum of families of POPs contaminating the aquatic systems. Important classes of POPs include chlorinated and brominated aromatics including polychlorinated biphenyls (PCBs), polychlorinated dibenzo-p-dioxins and –furans (PCDD/FS), polychlorinated diphenyl ethers (PBDEs) and different organochlorines pesticides (OCs) (Chun, 2011, Pellacani *et al.,* 2012; Amdany *et al.,* 2014). These compounds are called persistent because of longer half lives in a given media; however, their lives differ in soil, water and atmosphere.

POPs in aquatic systems are associated with toxicity, mutagenic, carcinogenic characteristics and these are the reasons they are hazardous to the biota and the environment. Furthermore, these compounds do not just pass through the rivers, but they become attached onto surfaces of particles of organic matter and clay particles (Wafo *et al.,* 2012; Amdany *et al.,* 2014). They then accumulate in sediments and are later released by various chemical processes and become available to the biota (Sukdeo *et al.,* 2012). These compounds bio-accumulate through the food web, and pose a risk of causing adverse effects to human health and the environment (Kang *et al.,* 2013)

Amongst the sources of POPs in the environment is the use of organochlorine pesticides (OCPs) in agriculture and for public health. While the use of these compounds was banned in developed countries in the 1970s and 1980s, developing countries still uses them due to low cost (Pellacani *et al.,* 2012). In Africa the use is mainly for agricultural pesticides and to control malaria by the use of Dichlorodiphenyltrichloroethane (DDT). These organic compounds affect the endocrine system and its normal functioning (Olujimi *et al.,* 2010, Kang *et al.,* 2013). The major DDT derivative, 1,1-*bis*-(4-chlorophenyl)-2,2-dichloroethene (p,p'-DDE) have been reported to bind on the androgen receptor on male rats (Kiece *et al*., 1995; Awofolu and Fatoki, 2004). Furthermore, OCPs are associated with human breast

cancer, liver cancer, testicular tumors and low sperm count in humans (Olujimi *et al.,* 2010).

Waste dumping sites are also sources of POPs. Domestic products such as electrical products contain polybrominated diphenyls ethers (PBDEs) and polybrominated biphenyls as constituents. These constituents are estimated to be between 5-30 % by weight of the product they make. When these consumer products are dumped in dumping sites, brominated fire retardants can become mobilized under certain conditions and leach into the environment (Daso *et al.,* 2013).

The leachate from landfills also presents a pollution problem for both surface and ground water (Daso *et al*., 2013). As the waste in the landfills breaks down, chemical components are mobilized and washed into surface and underground waters. Scrapyards have been shown to accumulate chemicals from breakdown of vehicle body parts, these chemicals are washed by rains every time it rains and that water ends in the rivers (Nekhavhambe *et al*., 2014). This makes the rivers to be the final destination of man-made chemicals and wastes (Baran *et al*., 2015)

1.4 Problem statement

Metals and POPs are chemicals of major concern to aquatic pollution (Tirkey *et al.,* 2012; Dennis *et al.,* 2013). The presence of metals and POPs is highly due to human activities; dumping of waste, industrial effluents, agricultural chemicals and consumer products (Sukdeo *et al.,* 2012). Metals and POPs disrupt natural chemical equilibriums, and ecosystems. Their toxicity is a problem to humans and other organisms (Fatoki and Awofolu, 2004). The Baynespruit River is classified as the most highly polluted river in the Pietermaritzburg region, and nationally, it is ranked in the top six most polluted rivers (Ramburran, 2014)

1.5 Rationale/justification of study

Water is a basic need. It is needed for drinking, cooking, industrial and agricultural processes, facilitates in waste removal, human recreation including swimming (Oluyemi *et al.,* 2010). Water supports living organisms; in fact, more than 90 % of our bodies are made up of water. However, contaminated water poses a threat for humans as well as wild life (Jackson *et al.,* 2010). The United Nations (UN) aims at achieving

water resource management of high quality for all human beings and the environment. Contaminated water is a precious resource lost (Nekhavhambe *et al*., 2014). Drinking water polluted by metals and POPs, and even used for irrigation purpose will have adverse effect (Adeniyi *et al.,* 2011; Lion and olowoyo, 2013,).

WHO (2016) provided statistics in which approximately 1.8 billion of the world population use a drinking-water source contaminated with faeces and by 2025, half of the world's population will be living in water-stressed areas. This highlights the need of the urgency and importance of maintenance, rehabilitation and protection of water systems from pollution. However, for maintenance, rehabilitation and protection of water to be successful, constant monitoring of water is necessary. Baseline concentrations of metals and POPs in aquatic systems need to be established (Bentum *et al.,* 2010; Ogola *et al*., 2011). This is the heart of environmental monitoring which is defined as the repetitive and continued observation, measurement, and evaluation of environmental or technical data to track changes over time (Vandecasteele, 2004). Monitoring of polluting substances is also important in the design of pollution control programs, and in understanding of the behavior of the pollutants as well as physical changes it goes through over a specific period (Park *et al.*, 2013).

Industrial effluents which are released into water systems intentionally and unintentional have been shown to be serious problem of water pollution. Depending on industrial activities surrounding the river environment, these effluents can contain oils, organic solvents, solid waste and other manmade chemicals. Once in the environment these compounds break down or converted into various substances, i.e. lubricating oils may release associated metals as well as organic pollutants. While metals and POPs are usually present in water in low concentration, plants and animals in aquatic environments have been shown to be able to concentrate trace metals in their tissue, and transferring them to secondary feeders (Crafford and Avenant-Oldewage, 2010; Mahakalkar *et al.,* 2013). This implies even slight emissions of pollutants in water system needs to be prevented at all cost.

Application of agrochemicals for faming also adds to water pollution, both ground and surface water (Su *et al.,* 2014). Communities practice agriculture to help themselves and fight poverty. However, application of mineral fertilizers and pesticides on the soils

in return pose a health threat to the same people. During rain and surface runoff these minerals and pesticides are transported into river systems where they bind into fine silt particles or become deposited on the river sediments. In turn they become available to the biota such as fish and humans then eat fish becoming exposed to substances such as OCPs.

Furthermore, irresponsible dumping of wastes on the river banks and nearby elevated grounds means waste can then be transfer in the river (Baran *et al.,* 2015). Domestic waste could have anything from food leftovers to mercury poisoning from electronic waste. Broken down electronic appliances means metals and POPs will be released into the ground then leach into the water. These polluting chemicals which may also happen to be toxic and carcinogenic need to be monitored in order to prevent them from transferring into environmental compartments (Daso *et al*., 2013).

Toxic chemicals in the river systems such as Pb and cadmium (Cd) are a concern to every environmental stakeholder. The nature and status of the river have major implications on the environments receiving them. If used for agriculture purpose, they can result in animal sickness, agricultural soil pollution as well pollution of the crops (Dennis *et al.,* 2013).

There is limited knowledge and data on levels of metal pollution and POPs in South Africa, especially the knowledge that covers all compartments of aquatic systems which are water, sediments and biota (Edokpayi *et al*., 2016; Sparks *et al*., 2017) . Fatoki *et al* (2002) reported on the high levels of Al, Cd, Pb, Zn and Cu in the Umtata River. Awofolu and Fatoki (2003) reported on the organochlorine pesticides residues in freshwater and sediments from Eastern Cape, South Africa, in which some endocrine disrupting OCPs such as 2,4-DDT, 4,4-DDT, 2,4-DDE, heptachlor, endosulfan and the chlordanes were detected. The aim of this study is to evaluate both metals and POPs in the water, the sediments and biota in the Baynespruit River in KwaZulu-Natal, South Africa. This will give an idea of the amounts entering the water column, the amounts remaining on the sediments as well as the amounts taken up by plants.

1.6 Research questions

Based on the above explanations on the problems due to aquatic pollution by metals and POPs, the following research questions are presented:

- Which trace metals are present in Baynespruit River and at what levels?
- Which POPs are present in Baynespruit River as well as the levels?
- Is the Baynespruit River posing any environmental threats and what is the extent of the threat?

1.7 Research aim and Objectives

The aims of this research was to determine and quantify metals and POPs. In addition, to determine the overall suitability of the water in the river using allowed trace metals and organic substances for human use.

The study objectives were:

1) To determine metals concentrations in water, sediments and plants.
2) To determine POPs concentrations in sediments.
3) To make deductions after results have been presented and discussed on the usability of water as per the Department of Water and Sanitation guidelines. .

CHAPTER TWO: LITERATURE REVIEW

2.1 Introduction.

Water in South Africa is a scarce resource (Crafford and Avenant-Oldewage, 2010; Nekhavhambe *et al*., 2014). As the population increases, more pressure will be applied on food resources in turn putting pressure on agriculture and irrigation. South African water supplies are used mainly for agriculture (60%), industries (10.5%), and municipalities (27%) (FAO. 2016. *AQUASTAT website)* [accessed on 28/03/2016]. The available water sources are being polluted by xenobiotic chemicals and over introduction of nutrients into them (Mmualefe and Torto, 2011). Water pollution is caused by various agents, but the major concerns are chemical pollutants (Ogola *et al.,* 2011; Rodda *et al*., 2016). Water is said to be polluted when it contains foreign materials which changes physical and chemical properties of water, and reduces it quality (Oluyemi *et al.*, 2010). The term water quality is an everyday used term though its implication or explanation may vary form one water user to another. One may include the appearance while the other may focus on taste. General properties that applies to water quality includes: adequate amount of dissolved oxygen, comparatively low organic matter, neutral pH, freedom from excessive amounts of infectious agents, toxic chemicals and minerals (Oluyemi *et al*., 2010). Water is a good solvent, this implies that most pollutants will be dissolved and become incorporated into the water. Dissolved polar pollutants are then transported by water and in the process binds and remain on sediments. Non polar pollutants leaves the water column quickly and be incorporated into solid particles

The focus of the literature will be on the methods used for the extraction of these pollutants from samples, bio-availability, quality control and their regulations.

2.2 Definition of Metals

Metals are defined as material that is typically hard, luster, good thermal and electrical conductivity, and malleable (Miessler and Tarr, 2011). Metal pollutants in the environment are these inorganic substances such as chromium, manganese, lead, and others that are present in the environment in low quantities. Their presence in environmental compartments is often increased by man-made activities. Some

metals, such as calcium and magnesium, are required by organisms for health and normal functioning, but they become toxic at high levels (Baran *et al.,* 2015). Others, are toxic by nature, even at low concentration they affect life and ecosystems. Some of these toxic metals, seems to play no essential role in environmental processes except increasing toxicity.

2.3 Some properties of metals.

Metals are non-biodegradable (Park *et al.,* 2013), therefore they are part of persistent pollutants in the environment. They exist in various forms depending on their environmental conditions; they can be solid (atoms) or aqueous solutions. In solution or when they bonded to ligands, some can exist in various oxidation states i.e. Cr^{2+} and Cr^{6+}. The availability and toxicity of metals depends on their states. Plants can only take up metals dissolved in water, while animals can also ingest metals irrespective of states as well as breathing in air containing metal particles (Crafford and Avenant-Oldewase, 2010; Razanica *et al.,* 2014).

The fact that metals exist in different forms and various states is very important for the aim of environmental monitoring. The measurement of the total metal is not a good indication of its effect and toxicity in environmental water systems. It is the speciation of metal in the water and sediments that is important (Fashola *et al.,* 2016).

2.4 Which term to use: Trace metals or heavy metals?

The two terms; heavy metals and trace metals seem to be used interchangeable in the studies of metal pollution. Some studies, uses the term heavy when reporting results for, Pb, Zn, Cu and Mn (Florescu *et al*., 2011; Imam, 2012). other studies use the term trace metals, and names Cd, Cr, Fe, Ni, Pb, Se, Co, As and Zn as metals (Arunachalam *et al*., 2014). So far it is notable that one metal i.e. Zn can either be a trace metal or heavy metal. Apart from trace metal and heavy metal, some studies drop the prefixes and just refer to inorganic pollutants such as, Cd, Pb, Zn, Cu and Ca as metals (Adeniyi *et al.*, 2011). Heavy metals are defined as electropositive elements having a density of greater than five (Craffod and Avenant-Oldewase, 2010). In this case most of the p-block elements become heavy metals. The definition implies heavy metal is loosely defined, but can be taken to be implying to the wide spread of

contaminants of the terrestrial and fresh water systems (Opaluwa *et al*., 2012). Since the term, trace refers to substantially low concentration of a substance, other studies uses the term metal to refer to the pollutant, and uses trace as denoting the amount of metals in aquatic systems (Olowoyo *et al*., 2013). In this work, in order to keep things simple, the term metal will be used as referring to all groups of metals.

2.5 Sources of metal pollution.

Sources of metal pollution can be divided into anthropogenic and natural sources (Olowoyo *et al*., 2013). Natural source includes weathering of rocks while anthropogenic activities include transportation, industries, mining, agriculture, and other activities that results in the release metals into the environment.

2.5.1 Natural sources

2.5.1 Natural weathering

Metals occur naturally in the environments, however in very low amounts. Anthropogenic activities are solely responsible for the elevated concentration of metals in environmental compartments (Sukdeo *et al.,* 2012). Natural bedrock may have metals on them, which leach to the natural environments during weathering (Sparks *et al*., 2017). Singo (2013) highlights cadmium as one of the metals that occur from forests fires, volcanic emissions and weathering of bedrock.

2.5.2 Anthropogenic sources

2.5.2.1 Transportation

Metal containing additives are used in the manufacture of fuels and lubricants. When these products reach the environment, metals are mobilized by breakdown of these products. Odiyo *et al.,* (2005), carried a study in which urban soils showed high contents of metals arising from vehicle exhaust, lubricants and tyres. In a similar study by Bentum *et al.,* (2010), metal pollution on roadside soil by vehicle emissions was reported. The study found high levels of Ni on vegetables planted along the road close to vehicle emissions. It was also found that metal concentration was high on the sampling sites closest to the road.

2.5.2.2 Industries

Also, industries such as textile, breweries and refineries discharge effluents which contains high amounts of metals which end reaching rivers. Some of these wastes are discharged by mistake while some are deliberate discharges of untreated waste water (Oluyemi *et al.,* 2010; Imam, 2012). Rivers passing through industrial areas therefore carry a risk of being polluted. Benning and Baird, (2001) reported such pollution in the Swartkops River Estuary in Port Elizabeth South Africa. This specific river flows through a highly industrialized area of Port Elizabeth. Consequently, high concentrations were obtained where runoff from industries and informal settlement entered the river (Benning and Baird, 2001). This emphasizes the need for continuous monitoring of rivers for metal pollution as well as the establishments of pollution baselines.

2.5.2.3 Mining

Mining activities also mobilizes metals. The tailings left in mine operations as well as extraction of mining products results in metals being released into river systems direct or indirect via surface runoff (Zhou *et al.,* 2008). The Mooi River catchment, in KwaZulu-Natal, South Africa, has been polluted by metals arising from mining activities in surrounding areas (Van Aardt and Erdmann, 2004). Mining also mobilizes metals into the atmosphere (Ayodele *et al*., 2014) and this also implies that more areas can be polluted other than those where mining is taking place, due to long range transportation of pollutants.

2.5.2.4 Agriculture

Application of metal containing chemicals in agriculture results in metal pollution. Pesticides and herbicides breakdown releases metals which then bind to soil and organic particles (Su *et al*., 2014). The application of inorganic fertilizers to supplement minerals also contributes to metal toxicity (Dennis *et al.*, 2013). The NPK fertilizer supplies Nitrogen, Phosphorous and Potassium to the soils. Various fertilizers are used to supplement other nutrients such as Calcium and Magnesium.

2.6 Basic chemistry of metals

Once metals are mobilized, they can follow different pathways of fate, they may become bound or adsorbed into other substances, such as soil organic matter, figure 2.1 (Dube *et al.*, 2001). Once bonded to organic matter and soil particles, these metals can then become available to plant roots and taken up by the plants. In this way they will start moving up the food chain.

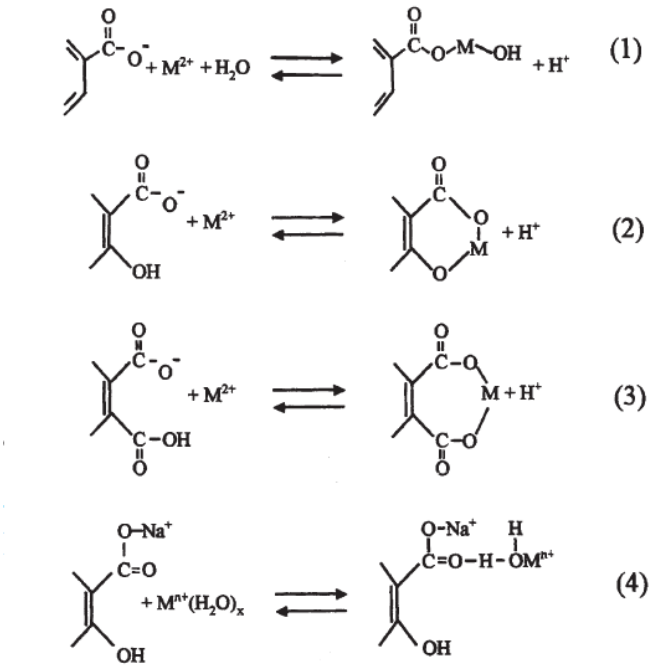

Figure 2.1: Mechanisms of complexation of metal with natural organic matter (extracted from Basta *et al*., 2005).

If the adsorption to the organic matter forms a strong interaction, the solubility and thus availability of the metal ion is reduced. Metal ions tend to form stable complexes with various ligands. The complexation reaction can be represented by equation 5.

$$Me^{m+} + L^{l-} \longleftrightarrow MeL^{(m-l)} ; K_{ML} \qquad (5)$$

This is a 1:1 metal to ligand complex formation, KML represent the stepwise formation constant of the complex. Complexes are not always 1:1, they may be polynuclear multi-ligand complexes. The general formation equation is shown by equation 6.

$$qMe^{m+} + rL^{l-} \longleftrightarrow Me_qL_r^{(q.m-r.l)} ; \beta_{ML} \qquad (6)$$

β_{ML} represents the overall formation constant of the complex (Evans, 1989). The formation constants represent the measure of how favorable the interaction is,

between the metal and the ligands. Stronger interaction will results in metals bonding to ligands, in this case in sediments for a long time and accumulate. This is the property that makes sediments to offer history of pollution in aquatic systems.

Metals may also react with particular species resulting in the change from solution into a solid, a process called precipitation equation 7.

$$Pb^{2+}_{(aq)} + 2I^{-} \longrightarrow PbI_{2(s)} \qquad (7)$$

Apart from reacting with substances and forming precipitates, being adsorbed to organic matter or forming complexes with ligands, metal ions can adsorbed by negatively charged clay particles (Dube *et al.*, 2001; Basta *et al.*, 2005). Soil consists of inorganic minerals, organic particles, and organic-mineral particles (Dube *et al.*, 2001). The inorganic portion of the soil is mostly composed of clay minerals and various oxides. Clay, which is the finer particles, <2µm, usually carries a negative charge. (Evans, 1989). Dube *et al.*, (2001), explains the formation of the negative charge as arising from two processes. The first part is due to the hydroxyl groups associated with minerals, these groups lose hydrogen which bonded to oxygen, with a weak covalent bond. This process is pH dependent. Higher pH favors the displacement of the hydrogen ion and can then be replaced by other metal ions such as Ca^{2+}, Al^{3+}, Pb^{2+} etc. The second process forming the negative charged is explained to be arising from the isomorphous ion replacement in the minerals. The clay particles are formed by silica tetrahedral layers (Figure 2.2). In this structure Al^{3+} can replace the silicon ion Si^{4+} because they have similar ionic radius. Ions such as Mg^{2+} and Fe^{2+} can then exist in the tetrahedral layers in the place of Al^{3+}. This ion exchange then results in a negative charge (2+ replacing 3+). This process is pH independent therefore it is the most prevalent processes. This implies that pH of environmental compartment such as rivers have to be monitored and controlled. If it allowed to be too acidic, this may favor mobilization of metals into solution and becoming available to plant roots. Not only would they become available to plant roots, but they can also be easily moved by rainfall to other environmental compartments, thus resulting in more pollution. Also, if the pH is allowed to be too basic, metals essential to plant health may precipitate out of solution thus making plants to show diffidence symptoms (Mahakalkar *et al.*, 2013). Apart from plants requiring certain

metals at low concentration for growth, plants also serve as receiving environment for metals. They are able to absorb metals, and concentrate them. These concentrated metals are then received by organisms feeding on plants. This exposes these organisms to toxic metals (Olowoyo *et al*., 2012). When the plants die and breakdown, and become organic matter, they release these metals back into the environment (Aryal *et al*., 2014; Malan *et al*., 2015)

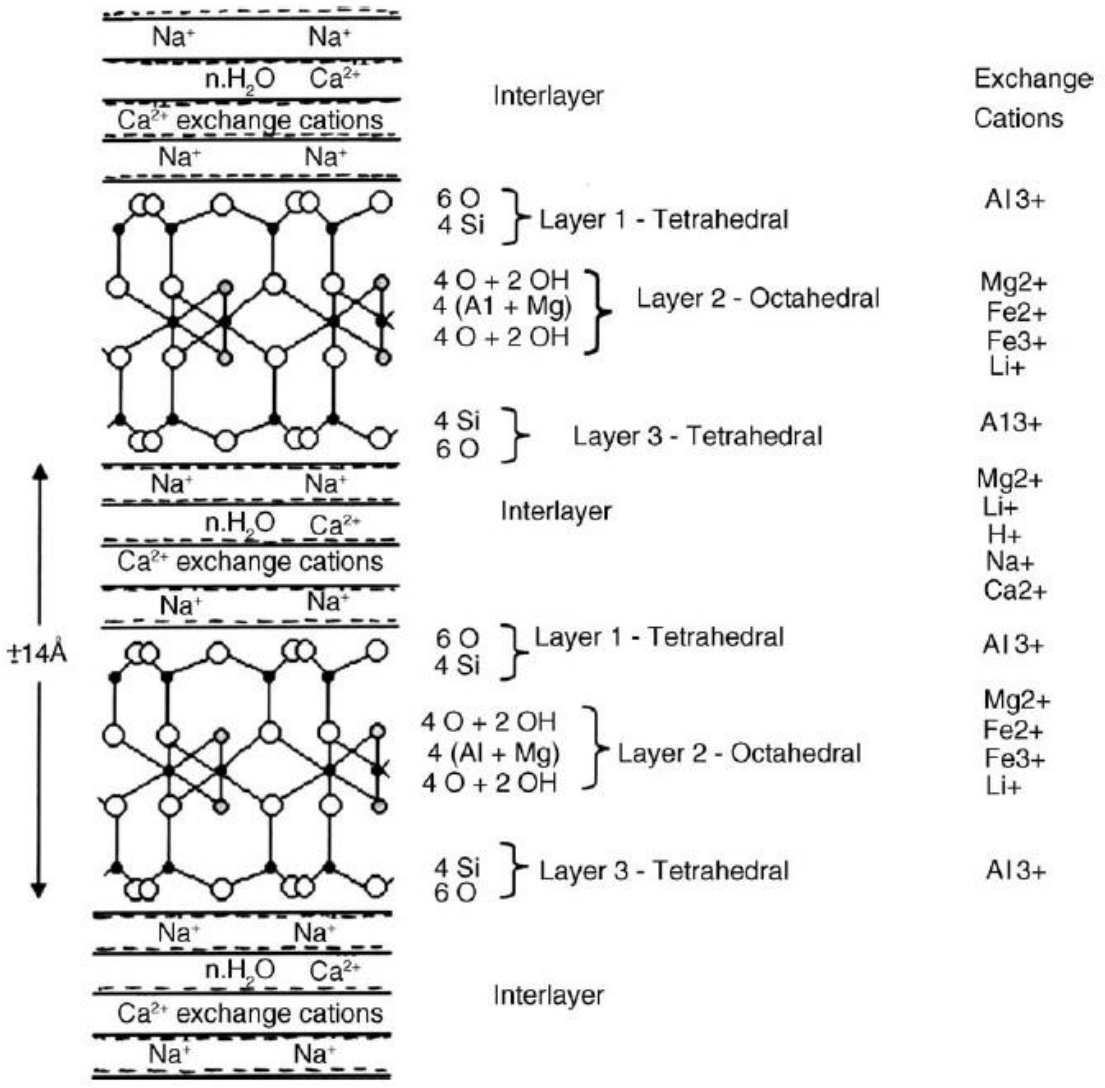

Figure 2.2: Tetrahedral structure of montmorillonite clay (From Tyagi *et al*., 2006)

In water, metals can exists in two fractions, the particulate and dissolved fractions. The dissolved fraction is considered as the available fraction. This dissolved fraction includes two forms of metals, the free metal ion and the complexed metal ion. The free metal from is called labile (Kumar *et al*., 2014). The complexed ion is bound in organic matter and immobilized in sediments (Pillay *et al*., 2014). During rainfall, the

particulate metal form increase due to surface runoff (Okonkwo *et al*., 2005; Kumar *et al*., 2014)

2.7 Effects of metals on humans and ecosystems.

Humans are exposed to metals in aquatic systems when they drink water, eat aquatic food, irrigate or swim in water. Inhalation of dust is also an important pathway for metal entry into the human body. The effects of metal pollution may either be sudden, for example animals dying in a short time, or they may be chronic, meaning effects increases with time and concentration in the body (Jackson *et al*., 2013). Various metals have been shown to be a health hazard to human life and wild life. Some of them are lead, arsenic, manganese, cadmium, chromium, zinc and copper.

2.7.1 Lead (Pb)

Lead, has been classified by the USEPA as a potential hazard to all life due to toxic effects at very low concentration and relatively bioavailable (Adeniyi *et al.,* 2011). In humans, lead is known for causing neurological disorders in the developing foetus and humans. Because these are developmental stages, the effects are modified behaviour and reduced IQs (Fatoki *et al.,* 2002). In fish, lead causes the coagulation of mucous surrounding the gills. Gills are used for gaseous exchange, the blockage results in suffocation and death. When humans feed on lead contaminated fish, lead would be transferred to humans. This is how contaminants are transferred from one organism to the other resulting in wide scale poisoning and deaths (Craffod and Avenant-Oldewase, 2010; Opaluwa *et al.,* 2012).

Exposure to lead is through the ingestion into the digestive tract and through the respiratory tract, once in the blood stream it is transported in the form of soluble salts, protein complexes or ions (Su, Jiang and Zhang, 2014).

2.7.2 Arsenic (As)

Arsenic is amongst inorganic pollutant in water systems. It has been reported that human exposure to high concentrations of arsenic in drinking water, results in usual dermatological manifestations that include; the raindrop pigmentation and skin cancer

(Abernathy *et al.,* 1999). These populations were reported in Taiwan, Inner Mongolia and China. In India, individuals who were exposed to elevated inorganic arsenic in drinking water manifested a range of symptoms such as peripheral vascular disease, non-cirrhotic portal fibrosis, lung disease and polyneuropathy (Abernathy *et al.,* 1999).

2.7.3 Manganese (Mn)

High levels of manganese in drinking water is more harmful to new born and children. If high levels are ingested during pregnancy, Mn may hinder intellectual development of the child (Buschaman *et al.,* 2008; Su *et al*., 2014).

2.7.4 Cadmium (Cd)

Cadmium has been classified by the International Agency for Research on Cancer (IARC) as a cancer causing agent on humans, and can be implicated on various cancers (Malan *et al*., 2015). Cd may affect the metabolism of Calcium, thus resulting in calcium deficiency. Calcium is responsible for bone structure. Calcium deficiency then results in poor bones and deformed cartilage (Su *et al.*, 2014). Exposure to Cd is by skin adsorption, ingestion and inhalation.

The general wellbeing and functions of ecosystems are adversely affected by metal pollution. This in turn destabilise the rest of the affected food chain, for example, the densities of nematodes communities in the Swartkops River Estuary were influenced by the degree of metal contamination in sediments. In turn all the organisms which depends on the nematodes for survival will were also affected. The end result is disturbed or destroyed ecosystems (Gyedu-Ababio *et al.,* 1999, in Benning and Baird, 2001).

2.8 Metal movement between environmental compartments

A study conducted by Roux *et al.* (1994) shows that a link of movement of pollutants between river, sediments and biota has been reported. In this study, water used to irrigate vegetables was tested for As, Fe, Al, Cd, Cu, Pb, Hg, Se, Zn, and Mn. All metals except for Cu, Pb, and Hg were detected in the fish. On the other hand, As, Cu, Zn, Mn, Al and Fe were detected in the plant tissue. Though metals in the plants were high in the roots compared to the leaves but the threat still exists. For some

plants, like sweet potatoes and potatoes, it's the roots that are eaten by humans not the leaves. Also famers sometime use the leaves as compost to provide organic matter, but since they would already be contaminated, they will also contaminate the soil again. Also, in a similar study by Odiyo *et al.,* (2005), which was aimed at investigating soil, vegetation and water contamination by metals, a correlation of soil and plant metals was observed, this is expected since the source of metals for both soils and plants will be the same. The concentration of metals was found to be high at a point where there was a direct sewage leak into the river. In fact, detection of metals in biological compartments, as well as human diseases has led to further investigations of the relationships in the environment (Dabrowski and de Klerk, 2013). Lead`s poisonous properties were notices as early as 200 B.C. with the early victims being the mineworkers and drinkers of wine containing lead as ingredient (Needleman, 2004). The responses of living organisms to toxic metals have also been used as indicators off pollution (Avidano *et al*., 2005).

2.9 Persistent Organic Pollutants

Persistent organic pollutants are organic, hydrophobic compounds, and therefore readily bind to particles (El-Shahawi *et al*., 2010). Hydrophobic refers to the nature of these compounds to avoid water or their water "fearing" properties (Amdany *et al.,* 2014). Hydrophobic compounds form aggregates which tends to excludes water, the example is the aggregation of oil molecules in a water-oil emulsion. These compounds are toxic by nature and persist in the environment due to their long half-lives (Wafo *et al.,* 2012). They are generally generated by man-made processes and are introduced into the environments in various ways (Doong *et al.,* 2008). They are also transportable by wind and water in the atmosphere by a process called Long Range Transport (El-Shahawi *et al*., 2010). This implies that POPs produced in one country can and up in another country. Table 2.1 shows the names of the POPs identified by the Stockholm convention and termed "the dirty dozen", and figure 2.3, shows chemical structures of these POPs.

Table 2.1: Twelve major POPs (*http://chm.pops.int* [accessed on 16/09/2014)

1. Aldrin	7. Hexachlorobenzene
2. Chlordane	8. Mirex
3. Dichlorodiphenyl trichloroethane	9. Toxaphene
4. Dieldrin	10. Polychlorinated biphenyls
5. Endrin	11. Polychlorinated dibenzo-p-dioxins
6. Heptachlor	12. Polychlorinated dibenzofurans

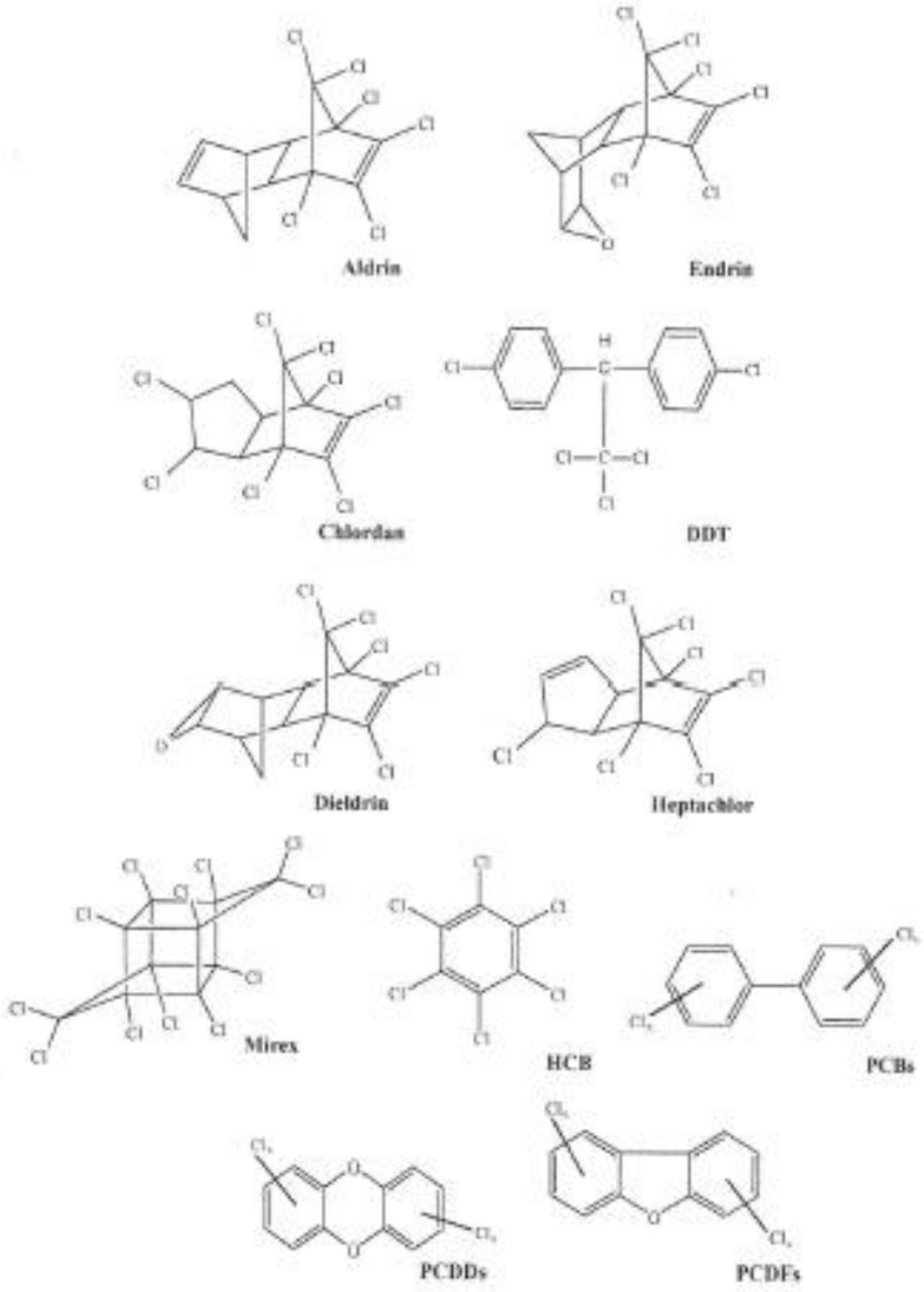

Figure 2.3: Structures of POPs referred to as “dirty dozen” (El-shawi *et al*., 2010**)**

POPs can be classified into two broad groups; intentional and unintentional POPs. Intentional pops include industrial compounds and organochlorine pesticides which are man-made and produced for a particular function. Unintentional are those POPs

which are produced as an unintended by product of combustion and chemical processes. These include polycyclic aromatic hydrocarbons (PAHs), dioxins and dibenzofurans (El-Shahawi *et al*., 2010).

2.9.1 Uses of POPs

POPs are used in various processes including agriculture, health/medicinal purposes and manufacturing (Rajendran *et al.,* 2005 in Doong *et al.,* 2008). They are used in manufacture of plastics. Their properties of high dielectric constants have made them ideal for use in fluids for high temperature processes, and to be used in heat transfer circuits for electronics and in high capacity transformers (Wright and Welbourn, 2002).

Pesticides are chemical or biological substances used in the eradication or control of pests (El-Shahawi *et al*., 2010). Mirex has been used in the United State to eradicate fire ants, termites and mealybugs. Also been used as one of fire retardants chemicals but was banned in 1977 (Makarewicz *et al*., 2003). Amongst other pesticides from the list of POPs are aldrin, chlordane, endrin and heptorchlor. Hexachlorobenzene were used as fungicides to treat seeds, and used in the industries to make ammunition, fireworks and synthetic rubber (EPA).

DDT is a widely used organochlorine pesticides, even though its use has been abolished in the 1970s and 1980s, some developed countries are still using them for agriculture and public health due to their effectiveness (Bouwman *et al.,* 2008).

2.9.2 Effects of POPs on humans and wild life.

Many of the POPs, especially PCBs and OCPs have been shown to disrupts membranes due to their small sizes and planar shapes (Wright and Welbourn, 2002). Also, there is evidence that these compounds affect the normal functioning of the endocrine system (Olujimi *et al.,* 2010; Pellacani *et al.,* 2012). The endocrine system is a control system which uses hormones for communicating changes in the body, it controls and coordinates body activities and maintains homeostasis (Olujimi *et al.,* 2010). One of organic compounds known to affect the endocrine system in the environment is DDT. In the environment, DDT is metabolized into Dichlorodiphenyldichloroethylene (DDE) and Dichlorodiphenyldichoroethane (DDD). The prevalent isomer, 2,4-DDE is able to bind to the androgen receptor in male rats

(Fatoki and Awofolu, 2004). Furthermore, OCPs have been linked to human breast cancer, testicular tumors and low sperm count.

Another group of compounds of environmental concern are the PBDEs. These compounds which are largely used as flame retardants and are not bound to the polymers they form. This enables them to be mobilized by environmental conditions and they leach out (Pellacani *et al.,* 2012). These compounds have been shown to be present in human tissue, blood and breast milk (Kang *et al.,* 2013). These compounds do not only affect humans at the point of exposure, they also affect unborn infants of mothers who are exposed to these compounds. Amongst defects detected are memory defects, cognitive dysfunction, decreased IQ scores and different neurological abnormalities (Pellacani *et al.,* 2012).

Prenatal exposures to di-ortho PCBs and PBDE have shown to influence birth weight in different directions. PCBs were found to be associated with higher birth weight while PBDE exposure resulted in lower birth weight (Lignell *et al*., 2013).

A study conducted by Bouwman *et al.,* (2008), reported on the study of the effects of OCPs on the eggshells in South Africa. Hexachlorobenzene (HCB), DDT, Hexachlorocychlohexane (HCH), Chlordanes and PCBs were all found in the eggs at detectable levels. The study also noted the existence of mirax, which was never licensed to be used in South Africa. This could be the case of long range transport of chemicals, meaning mirax used in other countries have reached South Africa or that there are some products entering the country which contain considerable amounts of mirax. The same study also showed that the thinning of eggshells of some birds is alarming and could be linked to some OCPs and PCBs.

2.10 Methods for determination of POPs and Metals

Determination of metals in water and sediments usually follows a method of acid digestion after proper sample preparation. The digested samples are then analysed for metal contents using the Atomic absorption spectroscopy (AAS) and inductively coupled plasma spectroscopy (ICP) (Oluyemi *et al.,* 2010; Imam, 2012). When studying metals in sediments it important to differentiate between total metals and those metals that are bio-available to plants (Malan *et al*., 2015). The use of concentrated acid to digest sediments yields results for all metal or total metals, therefore different methods for bio-available metals have to be used (Kumar *et al*.,

2014). One of the methods used for the bio-available portion of metals is the use of the 0.25M ammonium bicarbonate (NH_4CO_3) extraction method referred to as the ambic-2 method (Manson and Roberts, 2000). Another method used is the extraction method which uses 0.2 $mol.dm^{-3}$ Di-ammoium ethylenediamine tetra-acetic acid ($(NH_4)_2EDTA$) (Herselman, 2007). Both methods predicts only the metals would become available to plant roots as opposed to total metals which includes those that are in the form that is not available to plant roots.

Metal analysis for plant samples requires that plants be properly washed with deionized water to remove all metals adhering to the external parts of the plant. This has to be done because the aim is to measure metal taken up by plants from water. After washing, the plants must be milled and sieved using a desired pore sieve size. This is followed by acid digestion, then elemental analysis on AAS or ICP (Mahakalkar *et al.,* 2013).

POPs in sediments are determined by first drying up the sample at room temperature or freeze drying (Doong *et al.,* 2008, Nekhavhambe *et al.,* 2014). After drying, soxhlet extraction or solvent extraction was applied, followed by chromatographic clean-up, then analysis on Gas Chromatography, or Gas Chromatography mass spectroscopy (Doong *et al.,* 2008; Daso *et al.,* 2013; Nekhavhambe *et al.,* 2014).

2.11 Analytical instruments for metal and POPs analysis.

2.11.1 The inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES).

The ICP-OES is an analytical technique of choice for elemental analysis (Skoog *et al*., 2013). As with other analytical techniques, the ICP requires sample preparation prior to analysis. The sample must be presented in a suitable liquid solvent. However solids and liquids can also be introduced. The major components of the ICP are the sample intake tubes, the peristaltic pump, nebulizer, the torch, radio frequency generator, detector and signal processor (Tissue, 2013). Figure 2.4 shows basic layout of the ICP-OES instrument.

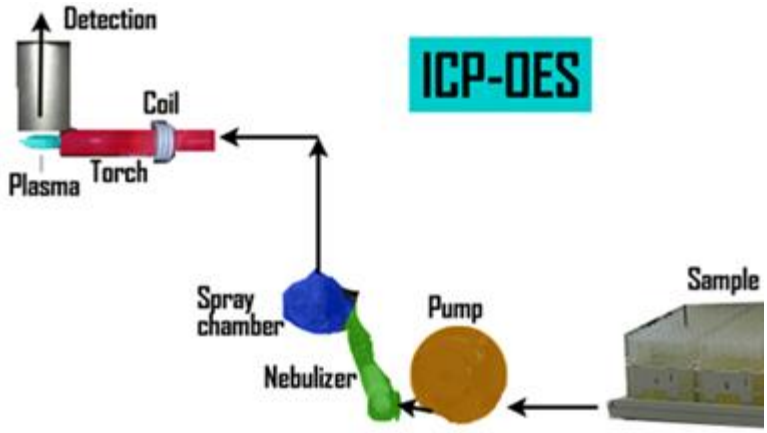

Figure 2.4: Schematic diagram of an ICP-OES (http://www.ru.nl)

For studies of metal in the aquatic environments samples are required to be acidified with nitric acid or other suitable acids. Strong acids such as hydrogen fluoride (HF) can damage the torch. As shown in figure 2.4, current ICP instruments are equipped with auto samplers, this allows for unattended analysis of samples. The tubes and the peristaltic pump function, is to introduce a sample into the instrument in a form of a continuous stream to facilitate atomization. Plasma and flame analysers fall in a class of contentious atomizers as opposed to discrete atomizers. Atomization is the process of converting a liquid sample into a gas-phase atoms and ions. The process of atomization starts with a liquid or solution sample (figure 2.5). The nebulizer converts the solution into a fine spray. The high temperature of the plasma evaporates the solvent, leaving behind a dry aerosol of particles. Further heat from the plasma courses the aerosol particles to be vaporized producing molecules, atoms and ions.

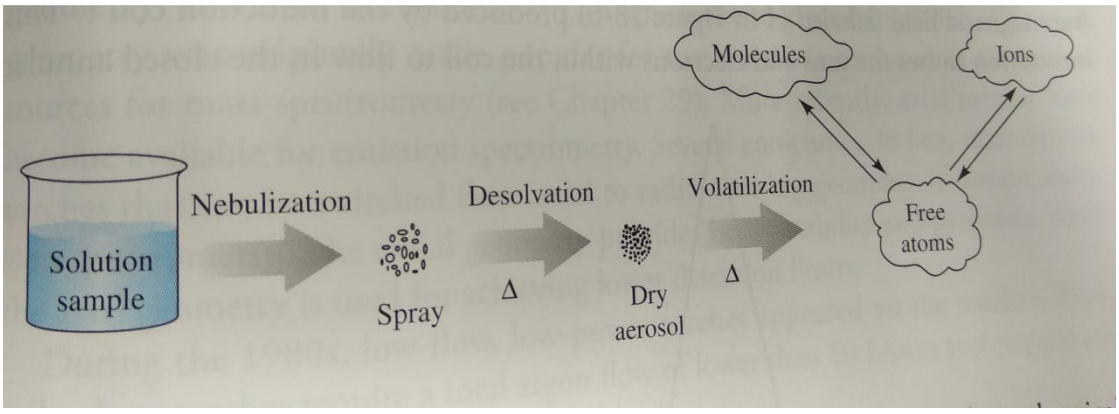

Figure 2.5: the process of atomization in ICP (Skoog *et al*., 2013)

2.11.1.1 Plasma source.

Plasma is defined as conducting gaseous mixture containing a significant concentration of ions and electrons (Skoog *et al*., 2013). In the ICP, this plasma is produced by the ionization of argon gas. The plasma is generated inside torch as shown in figure 2.6. The plasma source contains three concentric tubes in which argon gas flows. The top of the largest tubes of the three has an induction coil powered by a radio-frequency generator, which radiates 0.5 to 2 kW of power at 27.12 MHz or 40.68 MHz (Skoog *et al*., 2013). The tesla coil initiates the ionization of argon. The plasma temperature ranges from 6000 to 10 000 K. Skoog *et al*., (2013) reports the temperature of an ICP plasma to be 6000 to 8 000 K. These high temperature makes the ICP to be efficient since dissolution and vaporization is complete in a short time and atomization efficiency is quite high. This makes the ICP to be more efficient than flame based spectroscopy (Skoog *et al*., 2013; Tissue, 2013).

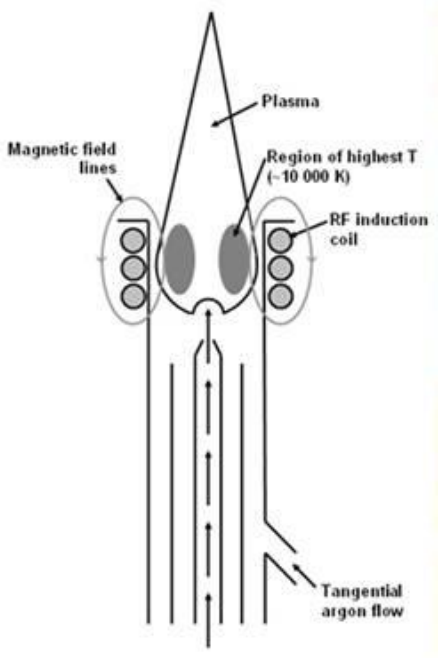

Figure 2.6: ICP torch showing argon flow, radio-frequency induction coil, and plasma (http://sites.cord.edu/chem-330-lab-manual/experiments/icp-aes)[01/11/2017]

2.11.1.2 Optical Emission Spectroscopy

Optical Emission Spectroscopy, determines the analytical concentration of analyte from the quantitative measurement of the optical emission from excited atoms (Tissue, 2013). This property differentiates the ICP-OES from AAS in that the signal from the ICP-OES comes from the excited atoms. Whereas for the AAS, signal comes from ground-state atoms as they absorb the light. The optics collects the emission from excited atoms and transmitted into a spectrometer. Since all atoms in a sample are excited at the same time, they also can be detected at the same time. This is a major advantage of the ICP-OES compared to the AAS which measures one analyte at a time (Tissue, 2013). While fast sequential AAS are now available and able to read analytes in one sample. This happen sequentially, one analyte at a time, for example, an instrument will analyse for Ca in a sample, finish this and move to analyse Mg, and so on. The ICP-OES would aspirate the sample once and provide all results for selected analytes.

2.11.2 Atomic absorption Spectroscopy (AAS)

The AAS is the widely used technique for elemental analysis due to its simplicity and low cost (Skoog, 2013, Tissue 2013). The major components of an AAS includes light source, sample atomizer, wavelength separator or monochromator and a detector (Figure 2.7).

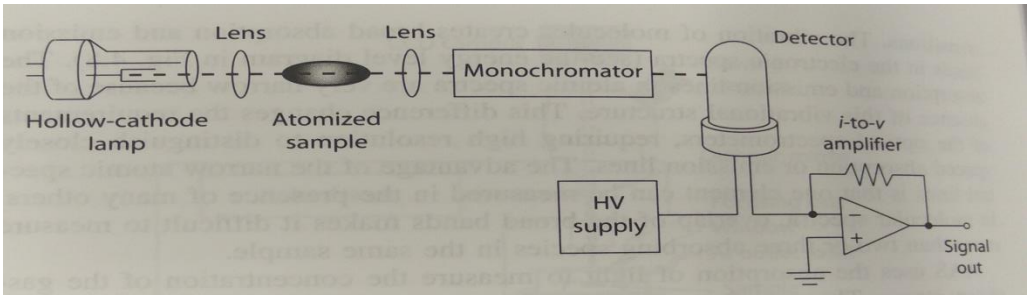

Figure 2.7: Basic components of an AAS (Tissue, 2013)

As it was with the ICP-OES, the AAS requires sample to be converted into a gas phase prior to atomization. This is done by the nebulizer which convert liquid sample into a fine mist. The atomization is provided by the flame. Depending on the application of

the AAS the fuel and oxidant can be any of the ones shown in table 2.2 (Skoog *et al*., 2013).

Table 2.2: Flames used in AAS and their temperature ranges (Skoog *et al*., 2013)

Fuel and oxidant	Temperature, ^{o}C
*Gas/Air	1700 - 1900
*Gas/O_2	2700 - 2800
H_2/air	2000 - 2100
H_2/O_2	2500 - 2700
**C_2H_2/air	2100 - 2400
**C_2H_2/O_2	3050 - 3150
**C_2H_2/N_2O	2600 - 2800
*Propane or natural gas **Acetylene	

Highest temperatures for the AAS flame are obtained when acetylene and a mixture of oxygen or nitrous oxide is used. It noticeable that the highest temperature of the AAS is only almost half the temperature obtained on the plasma of the ICP. The common light source for the AAS is a hollow cathode lamp (Tissue, 2013).

2.11.2.1 Hollow cathode lamp

The hollow cathode lamp shown in figure 2.8 is made from a tungsten anode and a cylindrical cathode enclosed in glass tube containing an inert gas at a pressure of 1 to 5 torr (Skoog *et al*., 2013). The cathode is made up of the element to be measured. The hollow cathode lamp provides the lights source which is absorbed by the specific atoms in the flame. The instruments measures the incident light before it passes though the sample, and measure this light again with the sample. The difference will represent the light absorbed by the sample. The concentration of the analyte can be worked out using beer-Lambert law relationship stating that the absorbance is directly proportional to the concentration of the absorbing species (Tissue, 2013).

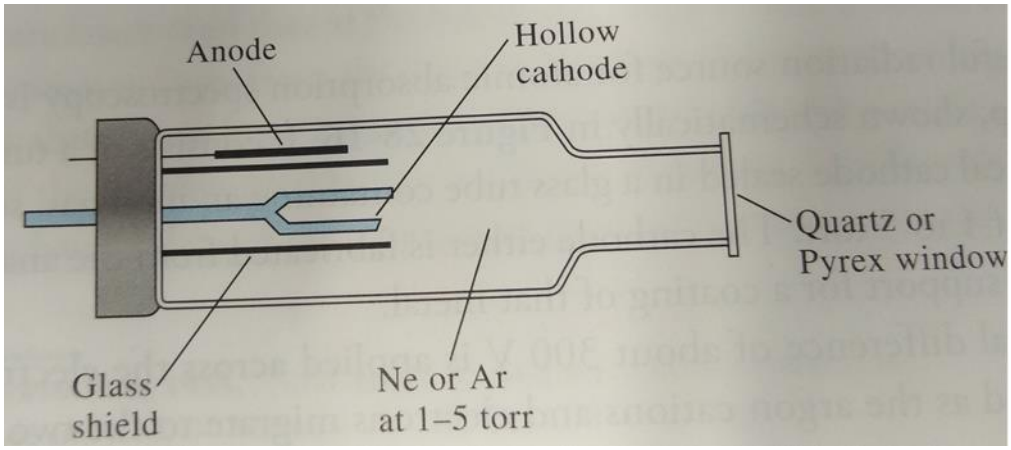

Figure 2.8: Hollow cathode lamp (Skoog *et al*., 2013)

2.11.3 Gas Chromatography Mass Spectrometry (GC/MS)

Gas Chromatography is a widely used technique for qualitative and quantitative analysis of volatile compounds (Skoog et al., 2007). The components of a vaporised sample are separated as they elute through the stationery phase. The gaseous mobile phase is the one responsible for the elution of the analytes. The stationery phase is held inside the column. There are two types of gas chromatography; these are gas-liquid chromatography (GLC) and gas-solid chromatography (GSC) (Tissue, 2013). Gas-liquid chromatography is a popular and a widely used technique and refereed in short as GC. Gas-solid chromatography is based on a solid stationery phase, and separation occurs as the analytes is physically adsorbed by the stationery phase. The GSC is not covered in this review. The main components of a gas chromatography technique are the carrier gas, injector port, oven, column and detector as shown in figure 2.9 (Skoog *et al*., 2013; Bayowa, 2014).

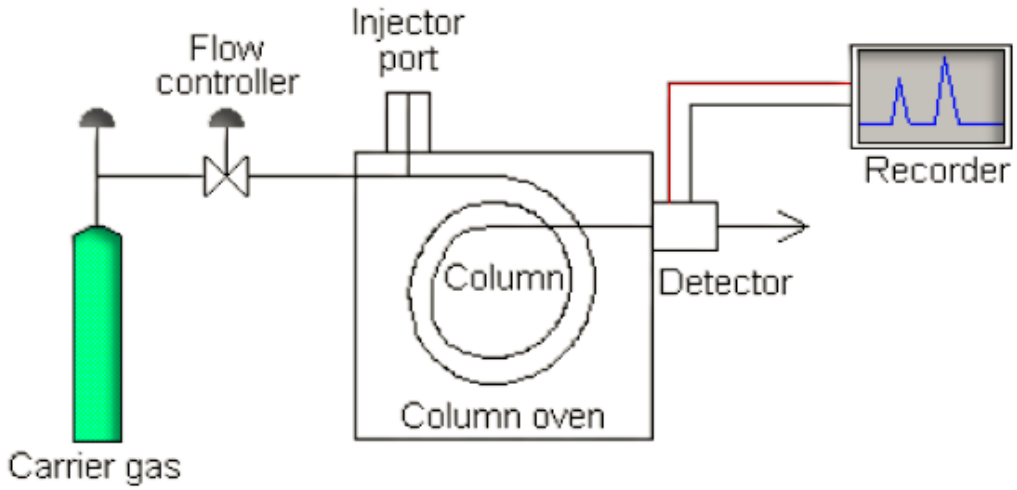

Figure 2.9: Components of a GC (Bayowa, 2014)

The injector port is used for inserting the micro-syringe containing the sample, and it is connected to the column. The oven is important in regulating and maintain required analysis temperatures. The oven is equipped with a fan inside to ensure uniform heating of the column. The column facilitates the separation of the compounds eluting inside. There are two types of columns that are generally employed in chromatography: the packed columns and the open tubular columns (or capillary columns) (Tissue, 2013). Packed columns are constructed from glass or metal tubing; their length is often 1 - 5 m long with internal diameters ranging from 2 to 4mm. these columns are packed with an inert support. This packing is usually prepared from naturally occurring diatomaceous earth, whose internal pore ranges from 2µm to 9µm (Skoog *et al*., 2007; Tissue, 2013). Capillary or open tubular columns have two varieties; wall-coated open tubular (WCOT) and Support-coated open tubular (SCOT). The internal diameters of these columns is 1mm or less. They are usually constructed of fused silica, which has a much higher degree of cross linking within the silicone-oxygen matrix than the ordinary glass. The silica used is of high purity with minimal amounts of metal oxides. The tensile strength of the silica tubing allows the construction of thin walled, flexible columns. Apolyimide coating is applied on the outside of the column for added protection. The flexibility allows the column to be bent into coils for fittings into ovens. Due to their popularity, Capilay columns have mostly replaced the packed columns (Poole, 2012; Skoog *et al*., 2013)

2.11.3.1 Detectors used in GC.

The detector is one of the important component of GC since it receives and amplify signals that will be displayed on the screen. Amongst the detectors that can be used is the Flame ionisation detector (FID), Thermal conductivity detector (TCD), Thermionic detector, Electrolytic conductivity detector, Photoionization detector, Fourier transform Infrared Red (FTIR) and Mass spectrometer (MS). The detectors are selected to suite the analysis based on selectivity and sensitivity.

2.11.3.2 Mass spectrometer detector.

Mass spectrometry is one of the most powerful detectors for gas chromatography (Skoog *et al*., 2013). The combination of GC and MS is known as GC/MS. Figure 2.10 shows the scheme of a mass detector. The sample is coming from the Gas Chromatography column. An interface is required to link the GC to the detector.

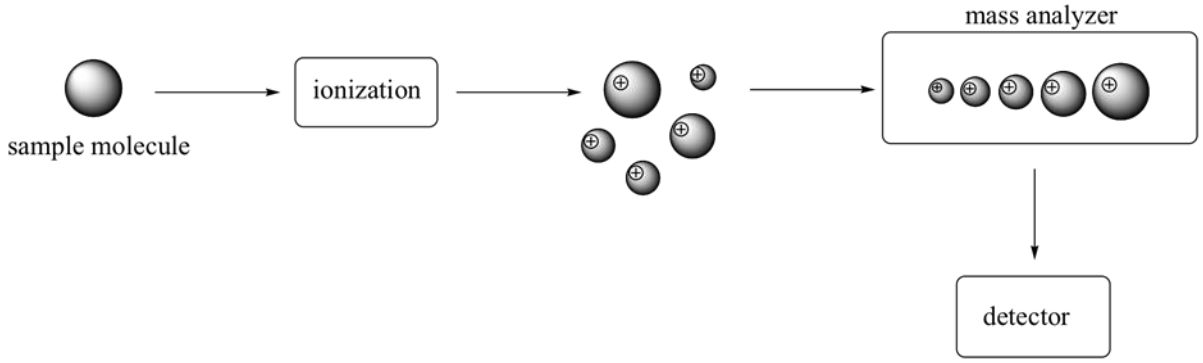

Figure 2.10: Scheme of mass spectrometer (https://chem.libretexts.org).

Figure 2.11 shows the operation of the mass spectrometer, the vaporized sample enters the MS via an inlet system. The operation of the spectrometer requires a vacuum system able to remove particles in the collision path. To enable this vacuum pump able to achieve 10-5 -10-8 torr is used. Form the inlet system the vaporized sample enters the ionization chamber, where they are ionized. The energy of the ionization source in molecular mass spectrometry is only enough to break chemical bonds in the sample molecules not to decompose it into atoms. This results in molecular fragments which can also be ionized. Charged molecules enter the analyzer and the uncharged species are pumped out by the vacuum pump. In the analyzer, ions are sorted according to their m/z values. The separated ions are then passed to

the detector, and a plot of abundance versus m/z values is produced by a data system (Skoog *et al*., 2013; Tissue, 2013).

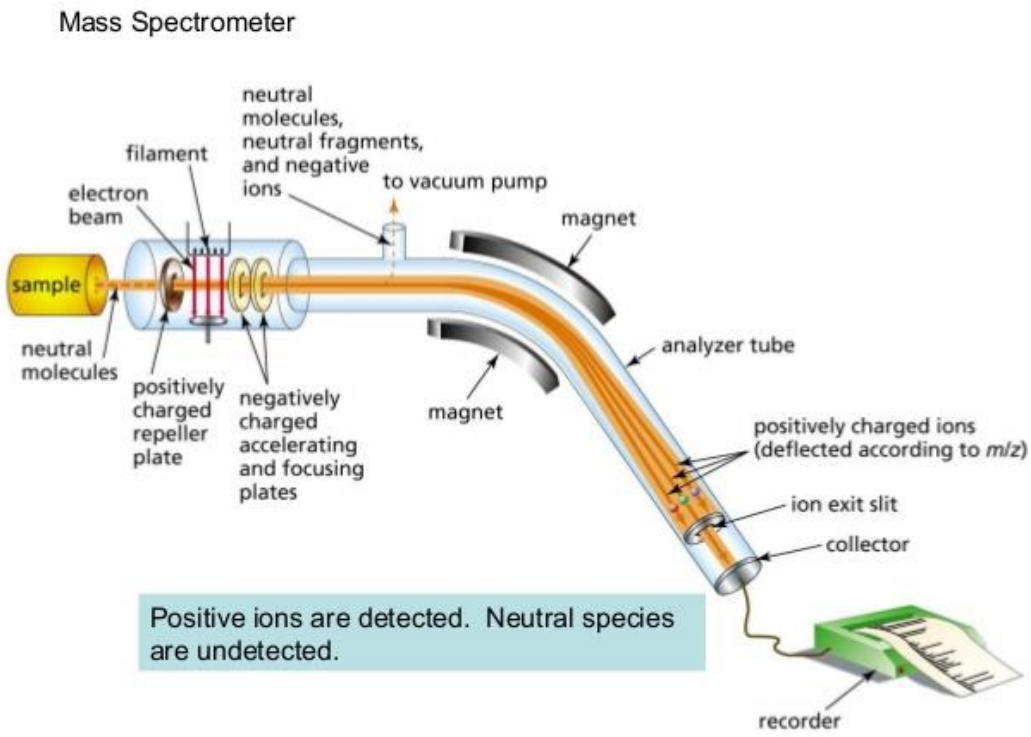

Figure 2.11: mass spectrometer analyser (https://chem.libretexts.org)

2.12 Regulation of chemical pollutants in water systems.

In order to maintain water quality, and maintain water as renewable resource, programmes to enforce water protection and regulations are required (Fuerhacker, 2009; Ogola *et al*., 2011). One of such regulation is the Stockholm convention. The Stockholm convention is a global treaty aimed at protecting human health and the environments from POPs (UNEP 2011). The convention was initiated in February 1997. The aim was to get the governments of different countries to agree to stop the use of products regarded as POPs. On May 2001 the treaty was signed and came into effects on May 2004 (Hardy and Maguire, 2010). Initially the Stockholm convention published a list of 12 POPs called “the dirty dozen” (table 2.1). Later on new nine POPs were added to the list (UNEP 2011).

The department of Water Affairs and Forestry in South Africa (now called Water and Sanitation) have published guidelines for classification of water according to use. The booklet is called Quality of Domestic Water supplies volume 1 of 1999. The document is jointly published by Water Research Commission and The Department of health. This guide allows water to be assessed and conclusion drawn whether water is suitable for drinking, food preparation, bathing or laundry. South Africa has published limits for selected metals in agricultural soils (Table 2.2) (Herseleman, 2007). The World Health Organisation (WHO) as well as other councils published maximum limits for selected metals as shown in table 2.3, (Awofolu, 2006).

Table 2.3: Soil maximum permissible limits (mg/Kg) for selected metals in South Africa and other countries (Herseleman, 2007).

	EU [a]	USA [b]	Germany [c]	Australia & New Zealand[a]	SA 1991[d]	SA 1997[e]
As	-	21	-	20	2	2
Cd	1-3	20	3	3	2	2
Cr	-	1500	400	50	80	80
Cu	50-140	450	135	60	100	6.6
Hg	1-1.5	8.5	-	1	0.5	0.5
Ni	30-75	210	75	60	15	50
Pb	50-300	150	300	300	56	6.6
Zn	150-300	1400	300	200	185	46.5

a – McLaughlin et al., 2000 b – EPA, 1995 c – Adriano, 2001
d – Nat. Dept. Health & Pop. Dev., 1991 e – WRC, 1997

Table 2.4: standards and guidelines (ppm) for trace metals in drinking water (Awofolu, 2006)

Metals	**[a]WHO**	**[b]CEC**	**[c]USEPA**
Fe	0.3	0.2	0.3
Al	0.2	0.2	0.05
Cu	1.0	0.1	-
Zn	5.0	-	-
Cd	0.005	0.005	0.005
Pb	0.05	0.05	0.015
Mn	0.1	0.05	0.05
Ni	-	0.05	0.1
[a]WHO = World Health Organization, [b]CEC = Community of European Council, [c]USEPA = United States Environmental Protection Agency			

CHAPTER THREE: RESEARCH DESIGN AND METHODOLOGY

3.1 Introduction

This study aims at determining trace metals and persistent organic pollutants in the Baynespruit River. This chapter presents the description of the study area, sampling and experimental procedures that were applied on the analysis of sediments, plants and water samples. Physical instrumentation will also be discussed.

3.2 Research design

Laboratory based studies are quantitative in nature (Mouton, 2001). While quantitative, they follow the positivisms research paradigm with quantitative methodology (Ngulube, 2015).

3.3 Study area

The Baynespruit River (figure 3.1a) is situated on the outskirt of Pietermaritzburg city, it starts from Northdale, and has a lot of tributaries and it passes the Sobantu village and informal settlements on its way to join the Msunduzi River (figure 3.1b). The project focused on the area of the river from Northdale through the Willowton Industrial Area (WIA). Two points on the other side of Sobantu where the river is joined by the Umngeni River were also sampled. This area is characterized by industries which release their effluents into the river as well as agricultural communities which uses agro-chemicals, manure etc. for their crops. In addition, there are various forms of human settlements (Table 3.1). Figure 3.2 shows the camera view of the river on site 3. Above this site is a bridge which is usually congested with traffic during morning and afternoon.

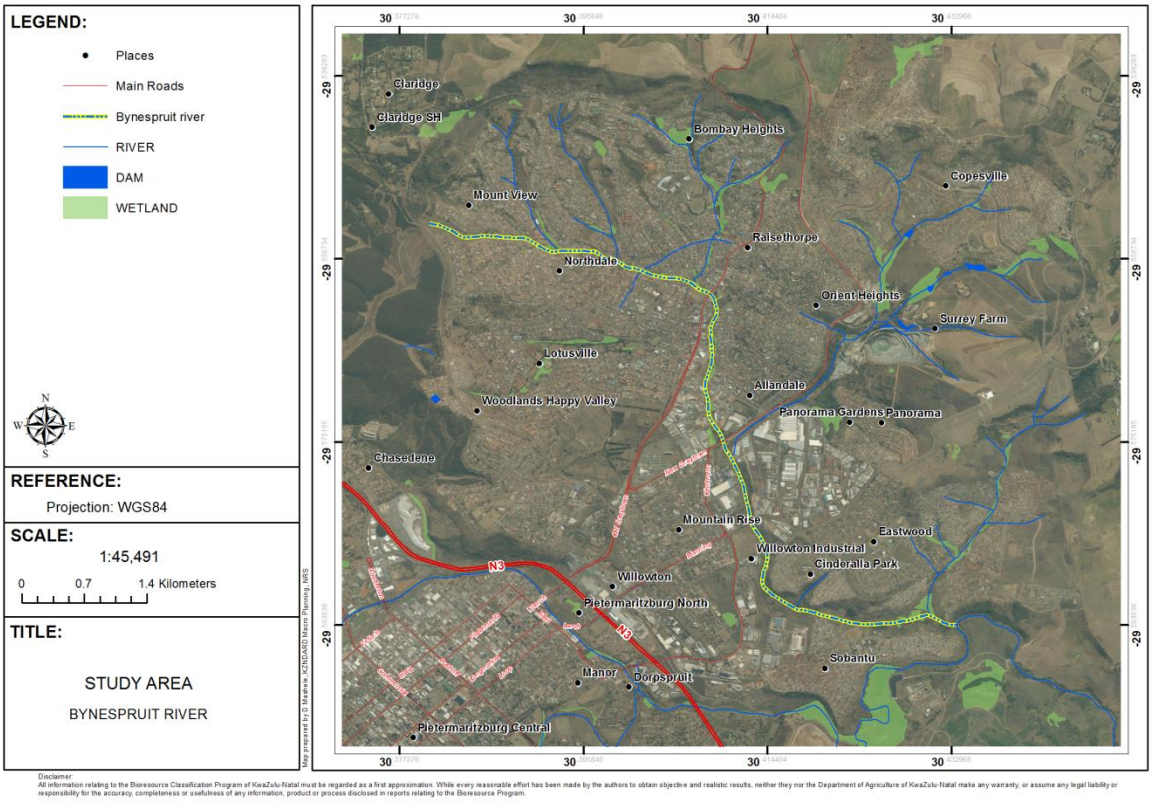

Figure 3.1a: Map of Baynespruit River (KZN DARD, Natural resources)

Figure 3.1b: Map of Baynespruit River (yellow) passing through formal, informal settlements and industrial areas (Google maps).

3.3.1 Sampling points description:

Table 3.1 sampling sites description and GPS coordinates

Site	Coordinates: Latitude Altitude	Brief description
Site 1	-29.55449 30.38805	Is mostly composed of urban dwellings with tar roads
Site 2	-29.56024 30.40853	Is right next to panel beaters. Various commercial activities are located in these positions.
Site 3	-29.57506 30.40990	Is located below a busy road. Few meters from this site, there is a stop site for trucks to rest, these trucks are usually abnormal loads. Also around site three, there are few building material hardware dealers which are associated with traffic of delivering vehicles
Site 4	-29.59775 30.42822	These two sites are adjacent to vegetable garden in the Sobantu Township. On one side of the river, there is a community vegetable garden, and on the other side is natural vegetation.
Site 5	-29.59772 30.4288	
Site 6	-29.59212 30.41835	Is located near the informal settlement. Immediately above this site there is a scrapyard as well as an open area for truck stop. There is a busy intersection with traffic congestion during peak hours.

Figure 3.2: Camera view of site 3 (Vincent Zuma)

Three samples for each medium were taken from each site making a total of 18 sediment samples, 18 plant samples, and 24 water samples. The sampling took place in two phases, one representing dry season (April 2015, autumn) and the other representing the wet season (November 2015, summer). For both sampling seasons, a total of 120 samples were taken. The sampling method used was the non-probability judgemental method (Baloyi, 2012). This type of sampling was chosen because it is simple, involves less cost, and samples are selected based on prior knowledge. It is well suited for research where resources such as capital and time are limited. Data obtained can be used as a starting point for more expensive projects (Fricker, 2012).

3.4 Sampling

3.4.1 Sampling of water

Sampling containers were washed with water and soap, rinsed with distilled water and soaked in 5% HNO_3 overnight. Water samples were taken using 500 ml plastic containers following DWAF 1996 guidelines as well SABS MA4 guidelines. Samples were then preserved with 5ml concentrated nitric acid except for the samples for physico-chemical properties.

3.4.2 Sampling of sediments

Sediment samples were taken using steel spoons, to avoid cross contamination, each spoon was used once, and sediments were then transferred into plastics, tied with an elastic band, and stored in a cooler box with ice.

3.4.3 Sampling of plants

Plant samples were sampled using pre-cleaned scissors and stored in brown paper envelopes. Plants were cut above ground to include stems and leaves, roots were not sampled. Samples were labelled at the sampling point to avoid mix up of sample.

3.5 Metal analysis

3.5.1 Sediment samples:

Sediments were spread on aluminium trays (figure 3.3) and placed in the drying room which is kept at room temperature until were completely dry, and later ground to pass through 1mm pore size of the sieve. All glassware was washed with soap and water, soaked overnight in 5% HNO_3 and after, rinsed with distilled de-ionised water.

Figure 3.3: Sediments samples in the drying room

3.5.1.1 Sample digestion for total metals

Ground sediment sample of 1g mass was placed in a 250 ml conical flask, 10 ml of concentrated nitric acid was added and mixture digested on a hot plate to near dryness. The residue was further digested with a mixture of concentrated acids containing HNO_3 (65%) (5 mℓ), HCl (5 mℓ) and $HCLO_4$ (5 mℓ) for 10 min at room temperature, and further digested on a hot plate in a fume hood to a volume of 5 ml and filtered using Whatman no1 filter paper, and made to 100 ml in a volumetric flask using distilled water (Odiyo *et al*., 2005).

3.5.1.2 *KCl (1M) extractable calcium and magnesium*

Ground sediment was scooped into sample cups using a 2.5 ml size scoop. A 1 *M* KCl solution, 25 mL was added and the suspension was stirred at 400 rpm for 10 min using a multiple stirrer. The extracts are filtered using Whatman No.1 paper. Five mL of the filtrate is diluted with 20 mL of 0.0356 *M* $SrCl_2$, and Ca and Mg determined by Atomic Absorption Spectroscopy (AAS) (Manson and Roberts, 2000).

3.5.1.3 Ambic-2 extractable potassium, zinc, copper and manganese

The Ambic-2 extracting solution consists of 0.25 *M* NH_4CO_3 + 0.01 *M* Na_2EDTA + 0.01 *M* NH_4F + 0.05 g L^{-1} Superfloc (N100), adjusted to pH 8 with a concentrated ammonia

solution. Of this solution 25 mL was added to 2.5 mL soil, and the suspension was stirred at 400 rpm for 10 min using a multiple stirrer. The extracts are filtered using Whatman No.1 paper. Potassium was determined by AAS on a 5 mL aliquot of the filtrate after dilution with 20 mL de-ionised water. Zinc, Cu and Mn were determined by AAS on the remaining undiluted filtrate (Manson and Roberts, 2000).

3.5.2 Plant samples:

Plant samples were washed with de-ionised water to remove dust and other particles and placed on aluminium trays (Figure 3.4). They were then dried in the oven at 105 ^{o}C overnight. Later, the plant samples were milled to pass through a 1 mm pore size of the sieve.

Figure 3.4: Washed plants in aluminium trays ready for drying

Plant digestion:

Plant material, 1.000 g of milled was placed in a 250 ml conical flask, 20 ml of HNO_3 (65%) and 8 ml of $HCLO_4$ (60%) was added in the flask, the mixture was then heated on a hot plate inside a fume hood to a final volume of about 5 ml (figure 3.5). Distilled water was added on the digest and filtered with Whatman no 1 filter paper, the filtrate was transferred into a 100 ml volumetric flask and made to the mark with de-ionised water (Odiyo *et al*., 2012).

Figure 3.5: Plant samples digested in a fume hood

3.5.3 Water digestion:

Water sample (100 ml) was transferred into a 250 ml conical flask, 5 ml nitric acid and three boiling beads (pre-cleaned with acid) were added, the mixture was reduced to about 20 ml under slow boiling, further 5 ml of 65% nitric acid was added and the mixture reduced to about 5 ml, the remaining clear sample was transferred into 100 ml volumetric flask and made to the mark with distilled water (Dwaf, 1992).

3.5.4 Determination of physico-chemical properties of water

The water samples which were not preserved by acid were analysed for pH and electrical conductivity (EC) using a Hanna pH meter and a Radiometer CDM 210 respectively. Both instruments are equipped with temperature probe for temperature compensation. Total alkalinity and chlorides were determined by the titration techniques following the methods used by the KwaZulu-Natal department of Agriculture and rural development (Manson and Roberts, 2000)

3.6 POPs analysis

3.6.1 Extraction of POPs

Air dried sediments were milled to pass through a 1 mm sieve. A laboratory analytical balance with four decimal places was used to measure 15.00 g of sediments and it was placed in extraction thimble and transferred to soxhlet apparatus shown in figure

3.6. Dichloromethane (DCM), 120 ml was added in the apparatus and the extraction carried out for 10 hours at 50-60 ^{o}C temperature. The extracts were then reduced to about 5 ml in a rotary evaporator, and later reduced to about 2 ml by gently blowing with air (Doong *et al*., 2008; Daso *et al*., Nekhavhambe *et al*., 2014).

Figure 3.6: Soxhlet extraction apparatus

3.6.2 Sample clean up.

A chromatographic column was assembled and packed with cotton wool, followed by 8 g of activated silica, and 2 g of copper powder (figure 3.7). The column was then washed with 15 ml DCM followed by 30 ml hexane. The extract was transferred into the column and eluted with 15 ml hexane, followed by 20 ml of DCM and hexane mixture (20:80). The collected extract was then reduced by rotary evaporator to about 1 ml, and dried with sodium hydrogen sulphate (Doong *et al*., 2008; Daso *et al*., Nekhavhambe *et al*., 2014).

Figure 3.7: Column chromatography used for sample clean-up

3.7 Chemicals/reagents used

- Hexane 99.9 % purity from Merck South Africa
- Hydrochloric acid 37% from Radchem
- Nitric acid 65 % from Ace Chemicals
- Perchloric acid 60 % from Ace chemicals
- Dichloromethane from Merck South Africa
- Pentachlorobenzene from Sigma Adrich
- Decachlorobiphenyl from Sigma Aldrich
- 100 ppm ICP multi-element standard from Merck South Africa
- ICP wavelength calibration standard from Merck South Africa

3.8 Instrumentation

3.8.1 Gas Chromatography Mass Spectroscopy (GC/MS)

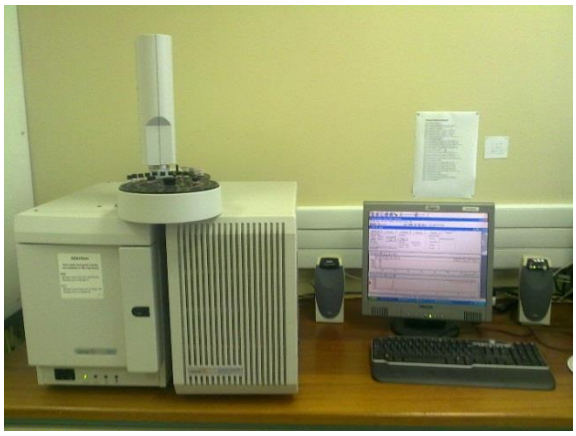

Figure 3.8: The pictorial representation of GC/MS instrument that was used

- The Varian GC 3900 fitted to MS detector Saturn 2100t (figure 3.8), with an auto sampler was used for the analysis. This GCMS runs with a Star software and is supplied with a NIST electronic library. The column in the GC was a VF-5ms, which is made of a highly inert 5% phenyl-methyl for increased sensitivity, accuracy and instrument uptime. This column has the lowest guaranteed bleed specification of 1 pA @ 325 °C (30 m, 0.25 mm, 0.25 µm).
- The GC was programmed as follows: initially temperature was held at 80^{o}C for 1 minute, heated from 80^{o}C to 150^{o}C at a rate of 20^{o}C/min, and then held at 150^{o}C for 5 minutes, heated from 150^{o}C to 200 ^{o}C at a rate of 20 ^{o}C/minute.

The carrier gas, helium, flow rate was held at 1 ml/min. a good resolution of the mixture of five PCBs was obtained (figure 4.1). As well as a chromatogram of OCPs (figure 4.1). They were then mixed together and injected in order to facilitate identification of the unknowns (figure 4.13 to 4.18).

3.8.2 Inductively Coupled Plasma Atomic Optical Spectroscopy (ICP-OES)

Varian Vista MPX ICP-OES (figure 3.9) was used for the analysis of elements in all samples. It is equipped with a quartz torch, nebulizer, auto sampler and a peristaltic pump. The plasma is generated by argon gas from a mini-tank supplied by Airflex Industrial Gases. The operating conditions of the ICP-OES are shown in table 3.2.

Table 3.2 ICP operating conditions

Instrument component	setting
Power (W)	1000
Plasma flow (L/min)	15
Auxiliary flow (L/min)	1.5
Nebulizer flow (L/min)	0.90
Pump rate (rpm)	15
Sample uptake delay (s)	30

Figure 3.9: The pictorial representation of the ICP-OES instrument

3.9 Quality control

For quality control the method of recoveries was used. Sediments and plant samples were spiked with 2 ml of 50 ppm multi-element standard. Water samples were spiked with 10 ml of a multi-element standard with various known concentrations. Pre-extracted sediments were spiked with 200 µl of PCBs, and 200µ l of the OCPs mixture. Then re-extracted following the procedure explained above.

3.10 statistical analysis

Microsoft excel and Genstat for windows (14th edition) were used for statistical analysis. The one way analysis of variance (ANOVA) was used to determine the significance difference of metal concentrations in different sites ($p<0.05$) (Gathumbi *et al*., 2013). The Pearson's correlation coefficient was also used to measure the correlation of metals in sediments and plants.

CHAPTER FOUR: RESULTS AND DISCUSSION

4.0 Introduction

This chapter presents results for the topic understudy. The results section is divided into six sub sections:

4.1 Quality control
4.2 Total metals in sediments
4.3 Bio-available metals
4.4 Metals in plants
4.5 Metals in water
4.6 POPs in sediments

4.1 Quality control

Quality control was carried out by spiking samples with known amounts of analytes and re-extracting them using the chosen method of digestion. Table 4.1 shows recoveries obtained after spikes were added in measured quantity of water sample. The spike of 5 ml of 100 ppm multi-element standard was added to 100 ml of pre-analysed water. This was done in triplicates. The values obtained are between 74.38 and 106.51%. These values are consistent with values reported with the findings by Okedeyi (2012) and Oluyemi *et al.* (2012). The lowest was for K at 74.38%. Recoveries for plants and sediments was carried out by spiking carefully weighed samples by 1 ml of 100 ppm multi-element standard, this was repeated by spiking with 1 ml of 50 ppm and 0.4 ml of 1000 ppm. Triplicates were analysed and the mean calculated. Table 4.2 shows recoveries for spiked plants and sediment samples. Recoveries for all reported metals ranged from 72 to 120% with Cr being the highest. These results also agree with those reported in the literature (Odiyo *et al.*, 2005; Arunachalam *et al*., 2014).

Table 4.1: Mean recoveries for spiked water sample and method limit of detection (LoD).

Recovery %	**Al**	**B**	**Ca**	**Cr**	**Cu**	**Fe**	**K**	**Mg**	**Mn**	**Na**	**Zn**
	102.80	93.95	96.02	93.03	94.33	98.80	74.38	99.94	94.76	92.79	106.51
LoD (ppm)	0.00730	0.0245	0.0110	0.00251	0.00507	0.0188	0.00864	0.00210	0.00539	0.0600	0.00401

Table 4.2: Mean recoveries and method Limits of Detection (LoD) for plant and sediment samples.

Element	LoD (ppm)	Recoveries plants (%)	Recoveries sediments (%)
Al	0.180	99.73	98.35
B	0.290	72.00	68.23
Ca	1.471	98.05	90.33
Co	0.040	77.43	75.66
Cr	0.040	78.42	120.11
Cu	0.022	87.47	77.10
Fe	0.176	96.13	100.08
K	4.775	124.74	90.92
Mg	0.098	98.68	87.28
Mn	0.040	82.03	98.03
Na	2.617	102.58	78.40
Ni	0.041	77.03	85.96
Pb	0.054	75.71	94.47
Zn	0.012	82.68	83.00

A pre-extracted sediment sample was spiked with a mixture of organochlorine pesticides and PCBs. The amount of the spike was 200 µl of 2000 ppm compound. The spiked sample was then subjected to soxhlet extraction following the same procedure applied to unknown samples. The chromatogram of the analysed extract is shown in figure 4.1. The peaks of the analytes were then identified and tabulated in table 4.3. These compounds which proved extractable by this method were then used as target compounds for analysing unknown sediment samples.

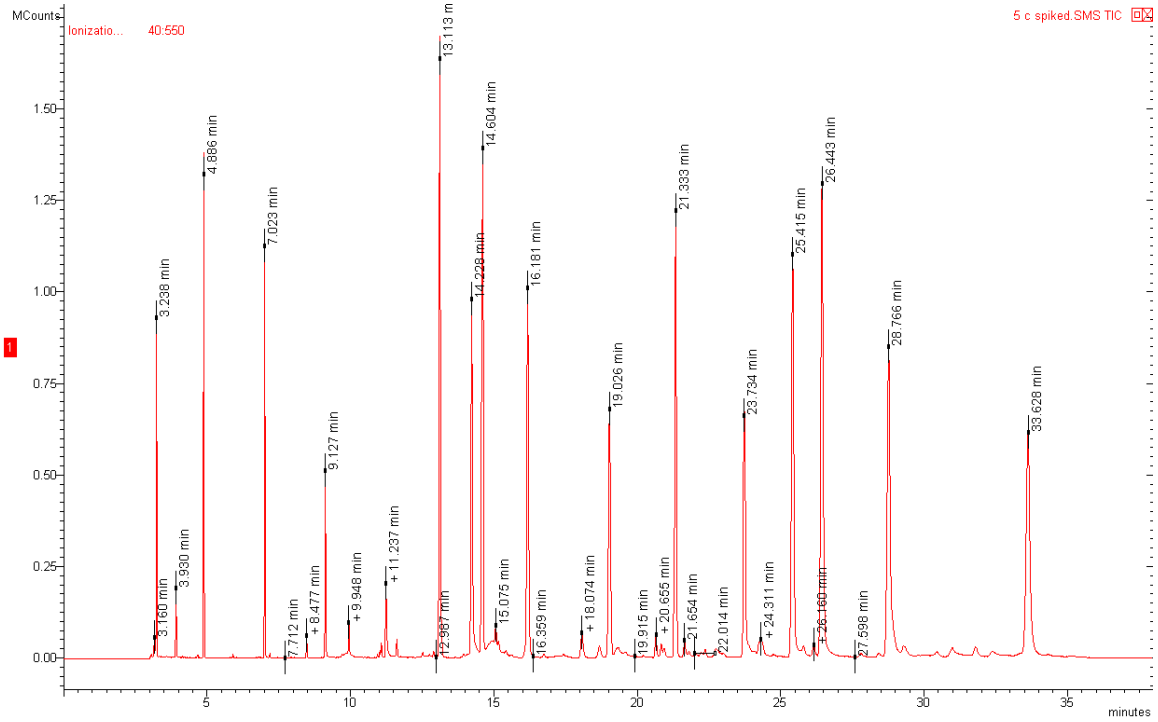

Figure 4.1: Chromatogram of sediment spiked with mixture of OCPs and PCBs

Table 4.3: Persistent Organic compounds identified after extraction and mean recovery values

Name	**Retention time**	**Recoveries (%)**
Alpha-BHC	13.113	101.56
Gamma-BHC (lindane)	14.228	100.64
Beta-BHC	14.604	93.55
Delta-BHC	16.181	74.34
Heptachlor	19.026	89.34
Aldrin	21.333	87.61
Heptachlorepoxide	23.734	51.77
Gamma-chlordane	25.415	75.10
Alpha-chlordane	26.443	69.02
4,4'-DDE	28.766	88.50
Endrin	31.052	13.26
4,4'-DDD	33.628	101.25

Recoveries were obtained by spiking a pre-extracted 15 g of ground sediments with 200 ppm of the OCP mixture. This was carried out in triplicates. The recoveries were found to be quite acceptable according to the EPA method 3630C, except for endrin (13.26%). Heptachlorepoxide was lowest was the lowest amongst the good recoveries at 51.77 %. The following set of standards were used for the calibration of the GC/MS 1.00, 2.00, 4.00, 8.00 and 16 ppm.

4.2 Total Metals in sediments.

Soil pH and organic matter play an important factor in metal mobility in soils and sediments (Lion and Olowoyo 2013; Sapek 2013). The pH values for the six sampling sites ranged from 5.23 to 6.16 (table 4.4) during the dry season sampling. This range on the scale falls on the acidic range. Acidity favours dissolution of certain metals making them bio-available (Omwoma *et al.*, 2014). Some metals are affected in such a way that they remain bonded to sediments particles and thus less bio-available (Baran *et al*., 2015). pH values for dry season sampling ranged between 5.23 and 6.16 while those of the wet season sampling ranged between 5.12 and 7.61 (table 4.5). The organic matter tends to form complexes with metal ions, removing them from solution, thus less bio-available. Organic matter ranged from 0.51 to 2 % (table 4.4) for dry season sampling, and ranged between 0.90 and 2.23 % for wet season sampling (table 4.5), on the sampled sites. Clay is also important in the binding of metals (Kumar *et al.*, 2014). Fine particles of clay behave as charged particles in the environment, this induced negative charge attracts and binds to metals making them less bio-available and less luckily to leach. For dry season sampling, clay content was between 20.83 to 38.5 % (table 4.4). For wet season sampling the clay content ranged between 21.17 and 50.50 % (table 4.5).

Table 4.4: Mean and standard deviation of pH, clay and Carbon values for 6 sites for dry season sampling

site	**pH**	**Clay (%)**	**Carbon (%)**
Site 1	5.95±0.0971	37.5±9.042	1.7±0.412
Site 2	6.16±0.251	38.5±2.291	1.842±0.361
Site 3	5.23±0.220	31.17±2.363	1.995±0.723
Site 4	5.35±0.129	25.33±12.85	1.03±0.723
Site 5	5.31±0.00577	20.83±2.843	0.51±0.169
Site 6	5.89±0.203	24.5±2.598	0.94±0.277

Table 4.5: Mean and standard deviation of pH, clay and carbon values for 6 sites for wet season.

site	**pH**	**Clay (%)**	**Carbon (%)**
Site 1	5.45±0.02	50.50±0.50	2.09±0.21
Site 2	6.05±0.01	34.50±1.32	2.23±0.30
Site 3	5.90±0.01	27.17±4.65	1.57±0.15
Site 4	5.12±0.01	28.00±2.00	1.09±0.24
Site 5	7.61±0.01	33.33±5.62	0.90±0.17
Site 6	5.72±0.04	21.17±3.01	1.93±0.48

For both sampling season pH followed the same trend among the sampling sites, except for 5 where the pH increased for the wet season (figure 4.2). The overall pH during both sampling seasons was not statistically different ($P>0.05$). However, during the dry season, the pH differences for all sites were statistically significant ($P<0.05$). For the wet season, pH differences for all sites were not statistically significant. The clay content was high in site 1 and site 5 for the wet season (figure 4.3). The difference in clay content was not statistically significant in both seasons. The carbon content was generally higher for the wet season sampling except for site 3 which was low (figure 4.4), however the difference was not statistically significant. Differences in clay and carbon for all sites during both seasons were statistically significant. These types of particles bind cations mostly and make them to be readily available when conditions are met, it is a reversible interaction (Baran *et al*., 2015).

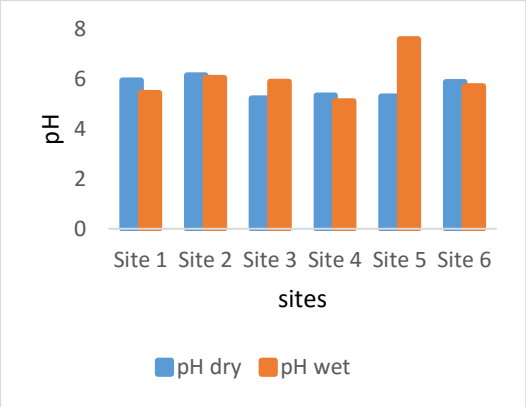

Figure 4.2: pH for dry and wet season sampling

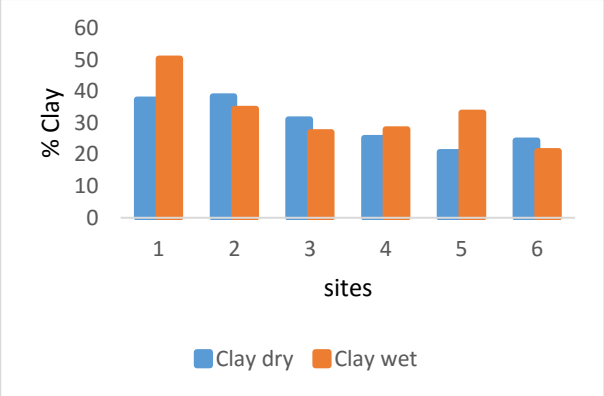

Figure 4.3: Clay content for dry and wet season sampling

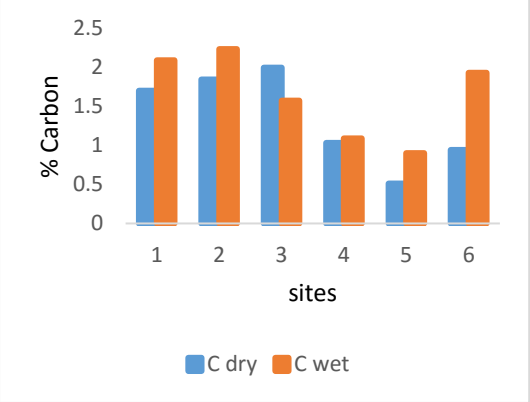

Figure 4.4: Carbon content for dry and wet season sampling

The mean concentrations of Al, B, Ca, Cr, Cu, Fe, K, Mg, Mn, Na, Pb and Zn for the dry sampling season are presented in table 4.6. Aluminium has a highest concentration of 21073 mg/kg on site 1, the overall range is 7 843 to 21 073 mg/kg. Aluminium is the most abundant metal in the earth crust (Silva, 2012). It is toxic to plants at high concentration which is favoured by acidic pH (Kidd and Proctor, 2000). Boron (B) has concentration ranging from 18.82 to 57.76 mg/kg. The highest concentration was on site 1. Fe has concentration range of 17609 to 29 835 mg/kg. The highest is on site 6 and the lowest on site 5.

Cr concentration range was between 48.21 to 78.62 mg/kg. The highest concentration was found on site 6 followed by site 3, these concentrations are approaching the maximum permissible Cr concentration in South African soils of 80 mg/kg (Herselman, 2007).

Table 4.6: Mean and standard deviation of metal concentration in sediments for dry season.

	mg/kg												
sites	**Al**	**B**	**Cr**	**Ca**	**Cu**	**Fe**	**K**	**Mg**	**Mn**	**Na**	**Ni**	**Pb**	**Zn**
Site 1	21073± 450.7	57.76± 10.78	63.48± 11.51	1760± 168.1	28.4+± 0.940	23981± 148.3	774.4± 20.27	1149± 60.03	572.5± 106.0	176.8± 17.23	16.88± 3.337	38.03± 7.707	86.56± 7.394
Site 2	13149± 936.0	51.07± 0.812	62.97± 6.026	1986± 309.7	32.34± 3.592	24255± 299.6	804.6± 59.76	1229± 61.45	496.7± 23.64	152.1± 4.924	11.09± 0.837	34.06± 8.467	77.88± 3.561
Site 3	12695± 3362	52.72± 2.494	77.72± 11.58	1866± 192.1	41.04± 8.728	25803± 1335	609.2± 186.0	1080± 115.8	496.4± 36.51	219.9± 78.96	15.48± 7.128	62.60± 13.83	155.2± 38.42
Site 4	10865± 4550	17.92± 9.149	48.21± 9.377	1262± 938.5	22.02± 14.33	17957± 3559	567.8± 179.8	932.9± 369.5	456.5± 203.5	113.1± 46.59	8.125± 4.549	23.26± 17.83	80.33± 48.60
Site 5	7843± 249.1	18.82± 2.762	50.06± 2.653	845.1± 20.61	17.04± 4.570	17609± 106.1	398.8± 73.14	751.3± 33.69	339.8± 22.61	112.3± 11.14	6.762± 2.067	18.79± 2.682	63.98± 0.931
Site 6	10400± 1240	57.53± 12.92	78.63± 8.769	1774± 99.43	24.71± 3.202	29835± 848.2	546.8± 73.14	1224± 169.2	470.8± 56.23	174.5± 10.37	10.14± 0.906	23.66± 3.19	114.4± 8.462
Limits*	--	--	80[a]	--	6.6[a]	50 000[b]	--	--	2 000[b]	--	50[b]	6.6[a]	46.5[a]

a- South African * maximum permissible

b – WHO -- not available

Both site 6 and site 3 are highly polluted and located in the high traffic zones, and both formal and informal settlements. This suggest that this increased Cr originates from anthropogenic activities such as sewage pipes and lack of sanitation in the informal settlements.

The range of Ca on the selected sites was from 845.1 to 1985 mg/kg, the highest was at site 2.

Cu concentration varied from 17.04 to 41.04 mg/kg. All the Cu values were higher than maximum permissible concentration of copper in SA soil of 6.6 mg/kg (Herselman, 2007). However, the concentration at site 3 was the highest. The site is located below a busy road. Few meters from this site, there is a stop site for trucks to rest, these trucks are usually abnormal loads. Also around site three, there are few building material hardware dealers which are associated with traffic of delivering vehicles. Cu has been shown to be high in areas associated with high traffic density and industrial activities (Bentum *et al.*, 2010; Olowoyo *et al.*, 2013). K concentration range varied from 398.8 to 804.6 mg/kg. Magnesium contents in all sites ranged from 751.3 to 1228 mg/kg. Magnesium is one of the essential elements for living organisms. Together with calcium they play an important role in uptake of elements in the soil.

Mn levels varied from 339.8 to 572.5 mg/kg, these levels are well within the WHO maximum limit of 2000 mg/kg (Chiroma *et al*., 2014). Sodium is one of the abundant metal in soils, on tested sites it ranged from 112.3 to 219.9 mg/kg. This metal affects soil structure and soil salinity. Site 3 has the highest concentration of sodium. Nickel concentration was found in the ranges of 6.762 to 15.48 mg/kg. The highest result was found at site 1. All the values are well within the SA maximum permissible limit of 50 mg/kg (Herselman, 2007).

Lead occurred in the range of 18.79 to 62.60 mg/kg, with site 3 recording the highest reading. The SA maximum permissible limit for Pb is 6.6 mg/kg. This means the highest concentration is more than 9 times the maximum. Excess lead could possibly be originating from the corrosion of pipes and paint from the building material industries (Jackson *et al.*, 2013). Lead can enter the environment from breakdown of paint and pesticides (Crafford and Avenant-Oldewage, 2010). Odiyo *et al.,* (2005), carried a study in which urban soils showed high contents of metals arising from

vehicle exhaust, lubricants and tyres. In a similar study by Bentum *et al.,* (2010), metal pollution on roadside soil by vehicle emissions was reported.

Zn concentration results for all 6 sampling sites ranged from 63.98 to 155.2 mg/kg. These values are higher than the maximum allowable limit for SA, which is 46.5 mg/kg. Site 6 had the highest concentration of Zn. Zn has also been shown to linked to high traffic density areas. Tyre ware releases Zn, which is used as a filler during the manufacturing process (Olowoyo *et al.*, 2013). This site also has sewerage leaking into the river (Gathumbi *et al.*, 2013). During the dry season sampling, site 3 had the highest for Cu, Cr, Pb and Zn.

The concentration of metals varied significantly on all six sites for some metals while others the variation was statistically significant. Al, B, Cr, Ca, Cu, Fe, K, Mg, Mn, Pb and Zn were found to have a difference which is statistically significance ($P<0.05$). On the other hand, Na and Ni had a statistically insignificance ($P>0.05$) difference on the six sites.

The good correlation (table 4.7) observed for metals during dry season sampling suggest that they came from the same point whether man-made or natural (Okedeyi, 2012).

Table 4.7: Correlation of sediment metals for dry season

correlation total metals and sediments properties dry season																
	Al	*B*	*Cr*	*Ca*	*Cu*	*Fe*	*K*	*Mg*	*Mn*	*Na*	*Ni*	*Pb*	*Zn*	*PH*	*Clay*	*Carbon*
Al	1.000															
B	0.535	1.000														
Cr	0.289	0.675	1.000													
Ca	0.601	0.715	0.693	1.000												
Cu	0.503	0.544	0.583	0.797	1.000											
Fe	0.344	0.842	0.864	0.760	0.579	1.000										
K	0.823	0.519	0.353	0.780	0.641	0.425	1.000									
Mg	0.603	0.670	0.678	0.935	0.659	0.802	0.783	1.000								
Mn	0.715	0.515	0.485	0.813	0.642	0.524	0.669	0.790	1.000							
Na	0.548	0.648	0.807	0.692	0.780	0.705	0.561	0.651	0.487	1.000						
Ni	0.807	0.555	0.653	0.682	0.706	0.503	0.719	0.622	0.661	0.855	1.000					
Pb	0.476	0.465	0.599	0.689	0.887	0.446	0.501	0.478	0.584	0.744	0.735	1.000				
Zn	0.274	0.451	0.768	0.659	0.814	0.666	0.309	0.552	0.490	0.821	0.624	0.823	1.000			
PH	0.394	0.802	0.399	0.574	0.308	0.597	0.542	0.538	0.300	0.316	0.311	0.208	0.047	1.000		
Clay	0.729	0.461	0.380	0.772	0.660	0.390	0.822	0.716	0.834	0.437	0.678	0.591	0.324	0.490	1.000	
Carbon	0.670	0.607	0.538	0.758	0.819	0.471	0.776	0.675	0.705	0.721	0.768	0.745	0.542	0.443	0.757	1.000

Table 4.8: Mean and standard deviation of metal concentration in sediments for wet season

	mg/kg												
sites	**Al**	**B**	**Cr**	**Ca**	**Cu**	**Fe**	**K**	**Mg**	**Mn**	**Na**	**Ni**	**Pb**	**Zn**
Site 1	24978± 2208	46.51± 2.306	42.80± 3.284	1994± 25.19	30.40± 1.496	20470± 248.3	1409± 164.2	1539± 92.08	946.0± 33.60	312.5± 29.14	14.79± 1.696	19.25± 0.921	90.29± 4.673
Site 2	15333± 606.1	43.21± 2.143	55.18± 0.730	2631± 127.8	48.50± 7.475	20135± 271.5	1170± 55.37	1553± 59.15	537.4± 21.29	300.4± 12.04	10.47± 0.681	33.27± 5.278	123.0± 7.305
Site 3	12135± 844.6	47.44± 0.838	86.42± 4.067	2171± 89.14	35.45± 2.435	21169± 96.59	687.7± 39.48	1313± 26.00	487.1± 6.321	250.6± 14.78	10.41± 2.105	48.17± 6.859	156.2± 5.399
Site 4	12025± 526.0	24.03± 0.770	53.83± 2.087	1280± 31.77	21.18± 0.702	14847± 313.7	652.9± 43.18	1010± 25.90	478.8± 15.87	226.1± 6.186	7.289± 0.633	23.44± 3.633	76.37± 2.379
Site 5	11311± 635.6	27.08± 1.474	62.35± 3.860	4334± 49.7	608.7± 136.4	15684± 372.2	728.9± 22.81	1441± 167.7	1081± 244.8	274.7± 2.607	7.877± 0.847	98.63± 3.166	154.9± 9.819
Site 6	14232± 816.1	70.31± 1.184	151.6± 5.654	2366± 93.87	39.83± 3.875	23649± 212.6	895.5± 135.1	1874± 72.27	827.3± 47.11	311.5± 6.300	15.76± 0.556	28.69± 1.510	194.0± 7.882
Limits*	--	--	80[a]	--	6.6[a]	50 000[b]	--	--	2 000[b]		50[b]	6.6[a]	46.5[a]

a- South African * maximum permissible

b – WHO -- not available

Table 4.9: Correlation of sediment metals for wet season

correlation total metals and sediment properties wet season																
	Al	*B*	*Ca*	*Cr*	*Cu*	*Fe*	*K*	*Mg*	*Mn*	*Na*	*Ni*	*Pb*	*Zn*	*PH*	*Clay*	*Carbon*
Al	1.000															
B	0.275	1.000														
Ca	-0.259	-0.141	1.000													
Cr	-0.289	0.783	0.010	1.000												
Cu	-0.348	-0.434	0.901	-0.151	1.000											
Fe	0.340	0.966	-0.157	0.646	-0.490	1.000										
K	0.915	0.317	-0.090	-0.264	-0.288	0.396	1.000									
Mg	0.329	0.809	0.342	0.598	0.009	0.758	0.487	1.000								
Mn	0.301	0.079	0.663	0.043	0.665	-0.006	0.261	0.500	1.000							
Na	0.642	0.639	0.259	0.252	-0.031	0.625	0.789	0.876	0.502	1.000						
Ni	0.643	0.866	-0.174	0.510	-0.414	0.834	0.608	0.778	0.296	0.784	1.000					
Pb	-0.500	-0.383	0.890	-0.061	0.924	-0.398	-0.429	-0.035	0.458	-0.129	-0.471	1.000				
Zn	-0.380	0.630	0.504	0.824	0.278	0.558	-0.256	0.658	0.264	0.331	0.328	0.412	1.000			
PH	-0.367	-0.262	0.973	-0.044	0.916	-0.267	-0.216	0.174	0.544	0.099	-0.324	0.951	0.457	1.000		
Clay	0.782	-0.227	0.035	-0.697	0.071	-0.118	0.729	-0.033	0.368	0.341	0.173	-0.123	-0.550	-0.017	1.000	
Carbon	0.534	0.626	-0.276	0.137	-0.549	0.711	0.637	0.495	-0.088	0.556	0.646	-0.575	0.034	-0.385	0.277	1.000

Table 4.8 presents metal concentration for wet season sampling. Figure 4.5a and 4.5b illustrates the variation of metal concentration in both wet and dry season sampling. The y axis is in logarithms in order to show both high and low values on the bar graph. Aluminium displayed an increase in concentration in the wet season compared to the dry season in all sites, except for site 3 which was almost equal in both seasons. However, the difference was not statistically significant ($P>0.05$). Boron is higher in wet season for site 1 to site 3, and then decrease in the remaining sites compared to dry season. The Boron dry season and wet season is also statistically insignificant. Ca was found to be high in wet season, and this difference was found to be statistically significant ($P<0.05$). Cr is higher in wet season in all sites compared to dry season, but the difference is not statistically significant. Cu was found to be high during wet season, and this was statistically significant. But site 5 shows a massive increase in Cu concentration. Fe is low in all sites for the wet season, and the difference was significant. K was found to be significantly higher in all sites for the wet season compared to the dry season. Mg, Mn, and Na were found to be higher in all sampling sites during the wet season compared to the dry season, the difference was statistically significant. Mn was very high for sites 5, site 1 and site 6 respectively. Na was generally very high in all sites. Ni was found to be almost the same for both sampling seasons. Lead decrease for site 1 to site 3 during the wet season. It then increases in site 4 to 6, though site 4 is very much equal in both seasons. The overall difference of Pb for the two seasons was not statistically significant. Zn was higher during the wet season, and the difference with the dry season was statistically significant. Highest concentration during the wet season was found on site 5 and 6.

The correlation for wet season sampling is poor (table 4.9) for most elements, this may suggest different additional sources compared to dry season sampling.

Dry season total metal analysis showed a high correlation of all metal with Carbon. This is expected as metals tend to complex organic matter. This is reported by many researchers (Chorom, 2013; Singo 2013; Aryal *et al.*, 2014). Correlation with pH was only observed for B, Ca, Fe, K and Mg. other metals demonstrate a weak correlation. Correlation with clay is high for Al, Ca, Cu, Mg, Mn, Ni and Pb.

During the wet season sampling, the correlation with clay was only found with Al, Cr, K and Zn. All metal demonstrated a high correlation with carbon except for Ca, Cr,

Mn and Zn. Ca, Cu, Mn, Pb and Zn showed a high correlation with pH, the rest of the metals were poorly correlated.

The difference in concentration of metals at all site for the wet season was statistically significant ($P<0.05$). This includes Na and Ni which were found to be insignificant during the dry season.

Cu, Cr, Pb and Zn were found to be high in the wet season. The concentration order for both sampling seasons was Zn > Cu > Cr > Pb. In a similar study by Ogola *et al.*, (2011), in stream 1 the following order was obtained, Cr >Cu >Zn >As> Pb, however values for this study were very high. The pollution by these metals is highly associated with industrialisation (Pillay *et a*l., 2014). Benning and Biard (2001) on a similar study Mn was 119.4 mg/kg, Zn was 45.0 mg/kg, Pb was 24.7 mg/kg, Cr was 11.9 mg/kg and Cu was 9.5 mg/kg. The currently study found Zn to be 96.37 and 132.46 mg/kg for dry and wet season respectively. Copper was 27.60 and 130.68 mg/kg for dry and wet season respectively. Cr was 63.5 and 75.37 mg/kg for dry and wet season respectively. Lead was 33.40 and 41.91 mg/kg for dry and wet season respectively. Mn was 472.11 and 726.50 for dry and wet season respectively. In comparison of these data sets, it is clear that the river understudy is highly polluted.

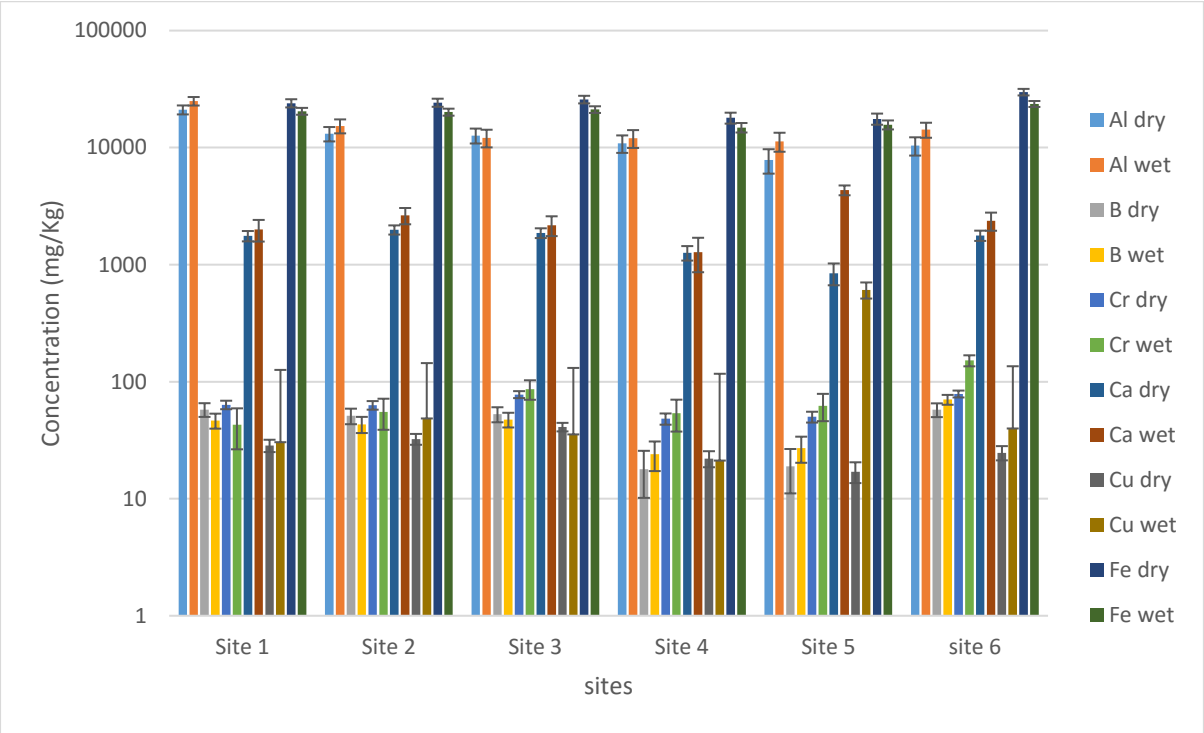

Figure 4.5a: Total metals in sediments for dry and wet season.

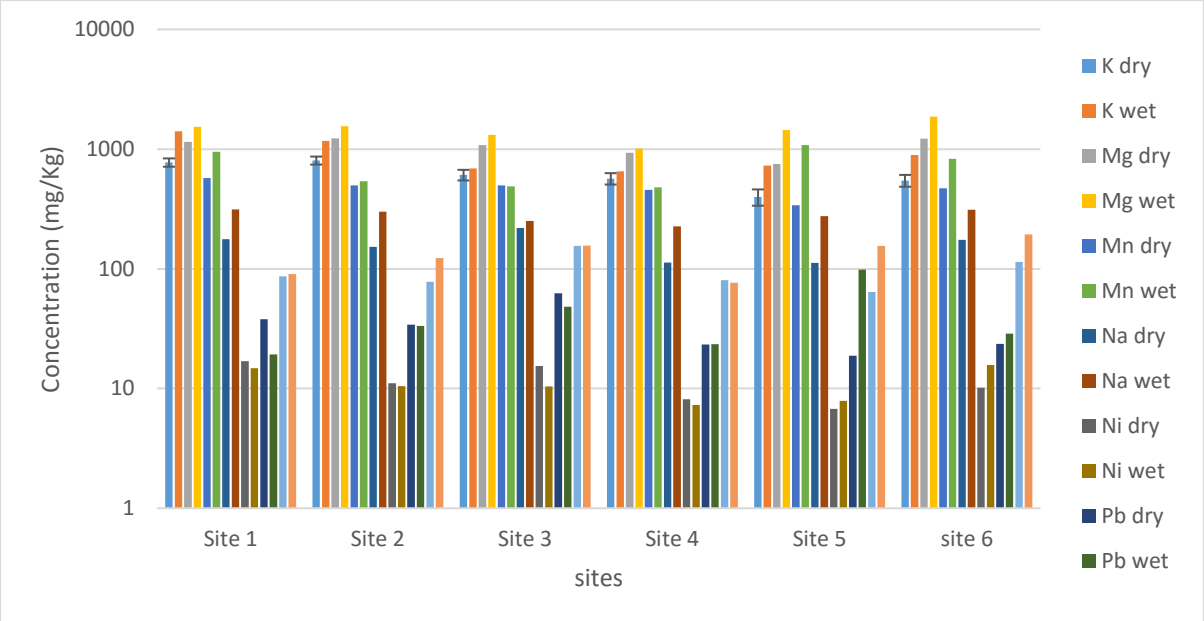

Figure 4.5b: Total metals in sediments for dry and wet season.

4.3 Bio-available metals in sediments

Bio-available metals differ from total metal in that they represent a fraction of metals that would become available to plants. Table 4.10 and 4.11 presents bio-available metals concentration for dry and wet season respectively. Metals of concern were Ca, Cu, K, Mg, Mn and Zn.

Table 4.10: Mean and standard deviation of available metals dry season.

	mg/kg					
Sites	Ca	Cu	K	Mg	Mn	Zn
Site 1	1551±11.93	5.4±0.5	138.7±65.73	317.1±24.58	10.33±4.041	15.90±1.015
Site 2	2348±450.6	8.967±1.274	80.33±5.508	353.0±56.67	6.667±2.082	11.93±2.658
Site 3	1822±113.2	23.17±15.48	39.33±13.58	236.0±21.28	7.333±4.163	29.70±10.62
Site 4	1039±481.9	4.267±2.579	68.67±11.55	293.7±140.1	51.33±53.27	21.37±16.23
Site 5	818.7±73.76	7.5±1.709	35.67±2.082	219.7±7.024	15.00±7.550	17.60±3.260
Site 6	1267±144.7	5.233±0.513	87.67±6.807	268.3±49.33	110.7±42.44	22.67±2.631

Table 4.11: Mean and standard deviation of available metals in wet season.

	mg/kg					
Sites	Ca	Cu	K	Mg	Mn	Zn
Site 1	1610±83.92	5.933±0.115	116.3±1.528	548.0±26.91	123.3±5.774	9.667±0.306
Site 2	1537±24.01	14.93±1.801	133.0±2.646	275.7±8.505	203.3±5.774	26.27±1.002
Site 3	1440±33.86	11.77±0.379	62.00±1.00	276.0±3.606	37.33±0.577	30.57±2.082
Site 4	1102±37.74	9.367±0.115	41.67±1.528	312.0±11.27	40.67±3.215	20.43±0.950
Site 5	1366±83.05	168.9±18.52	105.3±2.309	153.3±11.37	39.67±9.609	42.57±4.041
Site 6	1156±50.58	6.933±0.416	113.3±11.50	320.3±9.018	243.3±5.774	42.23±2.082

Dry season results:

Bioavailable Ca was found on the range of 818.7 to 2348 mg/kg. The low concentration was on site 5 and the highest on site 2. Cu concentration ranged between 5.233 to 23.17 mg/kg. The baseline Cu concentration range for SA soils is 0.84 to 10.6 mg/kg (Herslman, 2007). K concentration level occurred between 35.67 to 138.7 mg/kg.

Mg levels varied between 219.7 to 353.0 mg/kg, site 5 had the lowest concentration while site 2 had the highest concentration. Mn range is found between 6.667 to 110.7 mg/kg. Site 6 is the one with the highest Mn concentration. Zn ranges between 11.93

to 29.70 mg/kg. The baseline Zn concentration range for SA soils is 0.62 to 6.03 mg/kg (Herselman, 2007). All test sites are above the reported Zn baseline.

Wet season results:

Bioavailable Ca was found in the range of 1102 to 1610 mg/kg. The low concentration was found at 1012 mg/kg on site 4 and the highest at 1610 mg/kg on site 1. Cu concentration ranged between 9.667 to 30.57 mg/kg. K concentration level occurred between 41.67 to 133.0 mg/kg.

Mg levels varied between 153.3 to 548.0mg/kg. Mn range is found between 37.33 to 243.3 mg/kg. Site 6 is still the one with the highest concentration as it was during the dry season. Zn ranges between 9.667 to 42.57 mg/kg. The baseline Zn concentration range for SA soils is 0.62 to 6.03 mg/kg (Herselman, 2007).

Figure 4.6 shows the variation of available metals per site for the dry and wet season. The average of metal concentration shows that all metal concentrations were higher in the wet season compared to the dry season. It only Ca that was slightly less in wet season compared to the dry season. The increases metal concentration during the wet season support shows that rainfall results in surface runoff washing off metal pollution on roads and dust into the rivers (Dennis *et al*., 2013).

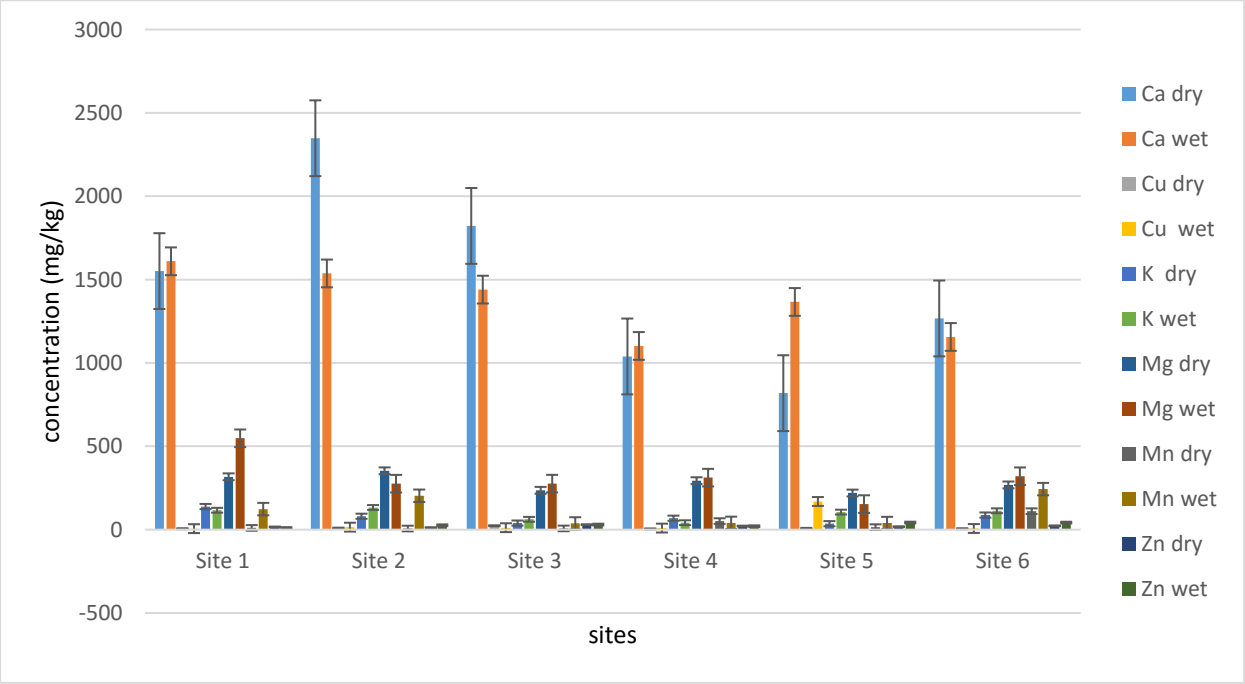

Figure 4.6: Bio-available metals for dry and wet season

During the dry season, the correlation analysis of available metals using ambic extraction shows a good correlation (r^2 >0.5) for Ca, Mg and Mn with clay (table 4.12). K, Zn and Cu shows a poor correlation. All tested metals show a poor correlation with pH except for Ca. Magnesium and Calcium are highly correlated with organic matter. Ca and Mg are the only metals that showed a good correlation. These two metals must have originated from one source.

In the wet season sampling, Ca, Mg and Zn show a high correlation with clay (table 4.13). All tested metals show a poor correlation with pH. K, Mg, Mn and Cu show a high correlation with organic matter. Also, K and Mn, Mg and Zn, Zn and Cu all display a good correlation with each other.

The concentration of K, Mg, and Cu were higher in wet season compared to the dry season, but the difference was not statistically significant (*P*>0.05). on the other hand, Ca was more in the dry season compared to the wet season, but also the difference is not statistically significant (*P*>0.05). Zn and Mn were high in wet season and the difference is statistically significant (P<0.05).

When comparing metal concentration on all sites, during the dry season sampling, it was found that the differences for K, Mg and Zn concentrations were not statistical significant. However, for Ca, Mn, and Cu the concentration differences amongst the sites was statistically significant.

Table 4.12: Correlation of bio-available metals and sediment properties for the dry season

correlation for sediments properties and available metals in the dry season									
	pH	*K*	*Ca*	*Mg*	*Zn*	*Mn*	*Cu*	*Clay*	*Carbon*
pH	1.000								
P	0.781								
K	0.456	1.000							
Ca	0.737	0.171	1.000						
Mg	0.347	0.315	0.515	1.000					
Zn	-0.308	-0.288	0.046	0.154	1.000				
Mn	-0.006	0.123	-0.385	-0.245	-0.039	1.000			
Cu	0.002	-0.273	0.317	-0.204	0.336	-0.246	1.000		
Clay	0.490	0.177	0.722	0.674	0.155	-0.550	0.110	1.000	
Carbon	0.443	0.218	0.745	0.489	0.294	-0.538	0.283	0.757	1.000

Table 4.13: Correlation of bio-available metals and sediment properties for the wet season.

correlation of metals and sediment properties for wet season									
	PH	*K*	*Ca*	*Mg*	*Zn*	*Mn*	*Cu*	*Clay*	*Carbon*
PH	1.000								
K	-0.233	1.000							
Ca	0.132	0.529	1.000						
Mg	-0.115	0.146	0.364	1.000					
Zn	0.068	0.114	-0.396	-0.780	1.000				
Mn	-0.240	0.714	0.051	0.248	0.140	1.000			
Cu	-0.040	0.139	0.021	-0.628	0.545	-0.397	1.000		
Clay	-0.265	0.355	0.732	0.612	-0.663	-0.087	0.051	1.000	
Carbon	-0.129	0.551	0.420	0.515	-0.286	0.714	-0.583	0.277	1.000

4.4 Metals in plants

Table 4.14 and table 4.15 presents metal concentration in plants for the dry and wet season respectively.

Table 4.14: Mean and standard deviation of metal concentrations in plants for dry season

	Mg/kg										
Sites	Al	B	Ca	Cr	Cu	Fe	K	Mg	Mn	Na	Zn
Site 1	926.8± 61.53	63.88± 43.63	16528± 319.6	14.62± 12.73	13.57± 5.890	1541± 132.6	1443± 3081	1528± 444.7	140.6± 4.65	465.7± 47.35	49.60± 1.979
Site 2	1085± 12.24	69.57± 19.80	43958± 1221	10.68± 5.842	24.29± 6.934	1724± 70.83	32270± 2805	3220± 135.2	93.75± 1.973	553.1± 25.30	106.8± 1.927
Site 3	551.4± 27.21	14.47± 3.133	15580± 807.6	11.31± 13.48	9.846± 5.419	1310± 147.6	7899± 2075	2344± 144.3	202.6± 11.18	243.9± 39.11	79.56± 5.528
Site 4	374.4± 21.04	27.02± 5.472	11448± 35.88	10.58± 6.614	4.954± 1.634	551.1± 27.34	5309± 815.0	1507± 77.40	159.2± 0.675	702.0± 33.63	28.01± 0.832
Site 5	622.0± 78.23	2.105± 1.157	11153± 159.5	5.037± 1.574	9.633± 4.560	1354± 176.6	7547± 378.8	3315± 129.0	650.9± 12.54	544.6± 16.77	52.15± 1.166
Site 6	226.7± 42.44	18.01± 8.527	11164± 2023	10.67± 1.393	9.633± 6.415	459.0± 65.65	11382± 3400	3802± 148.3	501.5± 92.26	3277± 587.2	45.76± 8.569

Table 4.15: Mean and standard deviation of metal concentration in plants for wet season

	mg/kg									
Sites	Al	B	Ca	Cu	Fe	K	Mg	Mn	Na	Zn
Site 1	174.1± 7.657	65.13± 67.74	13937± 615.5	7.880± 0.401	232.0± 15.46	12107± 3775	4141± 29.25	204.1± 8.402	867.0± 90.34	24.33± 3.112
Site 2	373.1± 9.475	143.9± 68.46	14141± 196.3	6.840± 0.160	590.9± 17.51	11043± 1716	5640± 72.75	141.6± 2.606	1668± 79.97	39.76± 0.762
Site 3	511.1± 18.06	21.08± 0.462	8181± 155.8	13.61± 0.541	771.1± 44.42	9946± 874.6	2737± 53.68	357.2± 4.584	5319± 162.2	60.84± 0.452
Site 4	789.6± 34.25	37.64± 22.17	12336± 199.5	8.568± 1.425	807.9± 11.15	8370± 1737	3571± 22.32	303.4± 3.503	2315± 43.88	49.87± 1.487
Site 5	384.5± 99.54	21.61± 0.508	10434± 161.3	9.763± 0.347	368.0± 16.78	6570± 1819	3841± 76.54	239.1± 6.333	2729± 111.7	37.98± 0.584
Site 6	792.1± 18.83	19.45± 2.260	8318± 188.2	9.043± 0.384	1001± 21.29	6816± 1940	3524± 60.34	480.7± 12.68	2643± 88.40	65.52± 2.037

Table 4.16: correlation of plant metals for dry season

plants dry correlation											
	Al	*B*	*Ca*	*Cr*	*Cu*	*Fe*	*K*	*Mg*	*Mn*	*Na*	*Zn*
Al	1.000										
B	0.675	1.000									
Ca	0.767	0.609	1.000								
Cr	0.141	0.370	0.083	1.000							
Cu	0.715	0.445	0.754	0.105	1.000						
Fe	0.924	0.452	0.623	0.152	0.665	1.000					
K	0.743	0.609	0.946	0.074	0.855	0.577	1.000				
Mg	-0.149	-0.301	0.190	-0.259	0.304	-0.065	0.292	1.000			
Mn	-0.471	-0.635	-0.513	-0.263	-0.161	-0.279	-0.396	0.618	1.000		
Na	-0.588	-0.204	-0.249	0.019	-0.113	-0.653	-0.052	0.550	0.467	1.000	
Zn	0.667	0.350	0.855	0.079	0.713	0.715	0.778	0.327	-0.318	-0.277	1.000

Table 4.16 show the correlation of metals detected in plants during the dry season. Most of the metals show a good correlation. This suggest that all the metals were absorbed by the roots form the same source (Okedeyi, 2012). Cr, Mn, Cu and Zn show a very poor correlation to other metals. All four of these metals are associated with anthropogenic activities.

Table 4.17: Correlation of metals in plants for wet season

	Al	B	Ca	Cu	Fe	K	Mg	Mn	Na	Zn
Al	1.000									
B	-0.355	1.000								
Ca	-0.516	0.643	1.000							
Cu	0.142	-0.473	-0.757	1.000						
Fe	0.900	-0.229	-0.588	0.266	1.000					
K	-0.502	0.217	0.459	-0.145	-0.328	1.000				
Mg	-0.424	0.742	0.776	-0.791	-0.360	0.321	1.000			
Mn	0.747	-0.585	-0.842	0.475	0.778	-0.446	-0.731	1.000		
Na	0.330	-0.410	-0.800	0.920	0.479	-0.208	-0.698	0.514	1.000	
Zn	0.815	-0.348	-0.803	0.525	0.939	-0.409	-0.550	0.855	0.708	1.000

Table 4.17 show the correlation of metals in plants during the wet season. While most metals show a good correlation, there are more metals with poor correlation compared to the dry season. During wet season plant are exposed to metals in sediments and those that are washed in by surface runoff.

Names of the plants that were sampled on each site per season are shown in table 4.18 and 4.19.

Table 4.18: Plants sampled in dry season

Site	**Plant**
Site 1	*Galinsonga parviflora*
Site 2	*Amaranthus*
Site 3	*Amaranthus*
Site 4	Sugar bean leaf
Site 5	Wondering Jew
Site 6	Wondering Jew

Table 4.19: Plants sampled in wet season sampling

Site	**Plant**
Site 1	Wondering Jew
Site 2	*Amaranthus*
Site 3	Wondering Jew
Site 4	Wondering Jew
Site 5	Wondering Jew
Site 6	Wondering Jew

4.20: WHO control limits of selected metals in medicinal plants (Shah *et al*., 2013)

Element	WHO limit (mg/kg)	recommended dietary intake (mg/day)
Fe	20	10-28
Cr	1.5 (permissible)	0.2
Zn	50 (recommended)	11
Mn	200 mg/kg	11
Ni	1.5 (permissible)	1
Cu	10 (permissible)	2
Pb	10	-

For site 1, during wet season, *Galinsoga parviflora* was sampled. Results obtained are comparable with similar studies shown in table 4.21; however, the results of this study are in the high end (Glowacka, 2012). Also, table 4.22 shows comparable results from another researcher, again these results highlights the high levels of contamination in site 1.

Table 4.21: Comparable results for *Galinsoga paviflora* (Glowacka, 2012)

Galinsoga paviflora	Mg/kg			
	Cu	Zn	Mn	Fe
	10.2	24.6	102.7	85.5

Table 4.22: Similar results for selected metals in *Galinsoga paviflora* as presented by Gyori *et al.*, 2014.

	Al	B	Cr	Cu	Fe	Mn	Zn
Mg/kg	21.8	10.0	0.58	7.0	40.0	18.2	33.6

In the wet season, *Amaranthus* was sampled on site 1 and site 2. This plant is an edible plant but Zn, Cu, Mn and Fe are very high above the World Health Organisation (WHO) limits for edible plants shown on table 4.20 (Opaluwa *et al.*, 2012; Lion and Olowoyo, 2013). On site 4, sugar bean leaves were sampled, though leaves are not eaten the high concentration of Zn, Mn, Cr and Cu means the beans themselves may have been contaminated by these metals. Sites 5 and 6, wandering Jew plants were sampled. While these are not edible the high concentration of Zn, Mn, Cu, Cr and Fe poses a threat to the food chain (Olowoyo *et al.*, 2012). The expected natural content of Zn in wild plants is stated to be between 15 and 80 mg/kg on dry weight basis (Rogóżand Nie-miec, 2010 in Glowacka, 2012). It is therefore clear that excess Zn in site 2 dry season sampling can be attributed to anthropogenic activities. These activities high traffic density. Zn which is used as filler during tyre manufacturing can be released due to tyre wear (Olowoyo *et al*., 2013). Washing of motor vehicles in the surrounding car wash services, application of pesticides, and application of Zn fertilizers such as Zinc sulfate can also release Zn into the environment. Such activities have been reported to be responsible for Zn mobilization in the environment (Gathumbi *et al*., 2014).

The notable high Mn at site 5 and site 6 during the dry season is way above the WHO limit of 500 mg/kg (Lion and Olowoyo, 2013). For medicinal plants, the maximum limit is 200 mg/kg (table 4.20). On site 6 during the wet season Mn is approaching the limit as well. This is well explained by the high levels of Mn in the water column which exceeds the DWAF limits for irrigation water.

For site 2, 5 and 6, similar plants were sampled, and when metal concentration were compared using single factor ANOVA, they were found to be different from each other, and the difference was statistically significant.

Amaranthus sampled on site 2 for both seasons has Boron concentration high in wet season, but the difference is not statistically significant. Al, Ca, Cu, Fe, K, and Zn concentration are all high in the dry season compared to the wet season, and the difference is statistically significant. Mg, Mn, and Na were all found to be high in wet season, and the difference was statistically significant. The increased rainfall in the wet season mobilises metals on the dust and road surface. Metals can also leach from sediments in contact with the roots. This implies that less metals will be absorbed. Also the high carbon person of the wet season compared to the dry season implies that more metals will bonded to the organic matter instead of being absorbed by plant roots.

The wondering dew sampled on site 5 also displays a variation in concentration for the metals understudy for the two sampling seasons. Al, Fe, Mn and Zn were found to be high in dry season compared to the wet season, the difference was statistically significant ($P<0.05$). B, Mg and Na were found to be high in wet season, and the difference was statistically significant ($P<0.05$). Ca, Cu, and K were high in dry season, but the difference was not statistically significant ($P>0.05$).

Different plant types were sampled due to the fact that site did not have same vegetation throughout the river length in both sampling seasons. This is important to note since plants accumulates metals differently (Olowoyo *et al*., 2013). Shuaibu *et al*., (2013), also states that plants accumulate metals differently and have different potentials of accumulating certain metals than others. For this reason, the results for *Amaranthus* on site 2 and 3 during the dry season, and site 2 for the wet season can be compared to each other. The results for *Galinsoga paviflora* are compared with results from the literature since it was found only during the dry season on site 1 only.

4.5 Metals in water

Table 4.23: Mean and standard deviation of metals in water samples during dry season

	ppm							
Site	**Al**	**B**	**Ca**	**Fe**	**K**	**Mg**	**Mn**	**Na**
Site 1	0.347±0.279	0.012±0.020	8.307±0.599	0.477±0.368	0.303±0.050	4.033±0.67	0.040±0.018	8.792±0.403
Site 2	0.064±0.099	nd	11.197±2.031	0.102±0.115	1.105±0.228	4.524±0.901	0.002±0.044	13.875±2.577
Site 3	0.079±0.069	0.267±0.463	5.269±6.622	0.252±0.310	1.056±1.458	1.796±2.228	0.044±0.054	11.586±14.161
Site 4	0.423±0.411	0.332±0.458	7.296±4.629	1.985±2.914	0.764±0.574	3.646±2.331	0.091±0.085	8.206±4.533
Site 5	0.170±0.148	0.012±0.012	6.008±2.428	0.382±0.116	0.493±0.216	2.956±1.169	0.057±0.023	6.206±2.636
Site 6	nd	0.018±0.022	7.655±4.669	0.294±0.224	1.407±0.946	2.845±1.754	0.099±0.062	13.644±8.375

Nd-not detected

Table 4.24: Mean and standard deviation of metals in water during wet season

	ppm							
Site	**B**	**Ca**	**Fe**	**K**	**Mg**	**Mn**	**Na**	**Zn**
Site 1	0.047±0.060	11.213±1.058	2.374±1.381	0.605±0.083	4.582±0.523	0.135±0.069	8.128±0.905	0.027±0.004
Site 2	nd	5.972±0.672	0.299±0.070	0.664±0.044	2.149±0.153	0.014±0.001	5.746±0.375	0.013±0.019
Site 3	0.034±0.058	7.315±3.698	0.366±0.102	0.891±0.498	2.120±1.166	0.034±0.017	6.962±3.659	0.008±0.005
Site 4	0.009±0.015	5.254±5.648	0.355±0.188	0.642±0.812	2.109±2.607	0.047±0.055	4.284±5.272	0.012±0.013
Site 5	nd	6.843±3.643	0.436±0.049	0.739±0.404	2.974±1.556	0.055±0.026	5.764±2.974	0.012±0.007
Site 6	0.002±0.003	8.393±0.585	0.554±0.090	1.293±0.251	2.588±0.438	0.129±0.025	9.082±1.590	0.018±0.021

Nd- not detected

Table 4.23 and 4.24 present metal concentration results in water for the dry and wet season respectively. The main differences in the two sets of results are that aluminium was not detected on the wet season as compared to the dry season. Zn was detected in the wet season and not in the dry season. These differences highlight the dynamic nature of river systems and the many factors that affect chemical composition at a given time. This variation also explains the high standard deviation observed in water sample results (Vega *et al.*, 1998). A study reported in Jackson *et al.* (2013), high metal concentration was reported during an influx of rain and less metal during dry seasons. This implies that long-term river quality monitoring is required for consistent data (Vega *et al.*, 1998).

Aluminium concentration ranged between 0.064 to 0.347 ppm. Site 6 was below detection limit. Boron concentration was between 0.012 and 0.332 ppm. Boron on Site 2 was below detection limit. Calcium ranged between 5.269 and 11.197 ppm. Site 2 had the highest concentration. Iron ranged between 0.102 to 1.985 ppm. Highest concentration was on site 4. K concentration occurred between 0.303 to 1.407 ppm. Mg was between 1.796 and 4.524 ppm, highest concentration occurring at site 2. Mn was low, the highest being site 6 with 0.099 ppm. Sodium ranged was between 6.206 and 13.875 ppm.

During the wet season sampling, B was barely detectable. Ca showed an increase for all sites except for site 2, compared to dry season. Iron also showed an increase for all sites, except for site 4 which dropped drastically. Mn also increased in the wet season. Mg was very much the same as the dry season.

Boron and Ca were found in high concentration in dry season compared to wet season, but the difference was not statistically significant ($P>0.05$). Fe and Mg concentrations were high is wet season, though the difference is not statistically significant. There was no difference for K and Mn in terms of seasons. Na concentration was high in the dry season sampling and the difference is statistically significant ($P<0.05$).

The average metals on all sites for the wet season follows this trend

Zn = B < Mn < Fe < K < Mg < Na < Ca

During the dry season the average follows this trend:

Mn < B < Al < Fe < K < Mg< Ca < Na

Al, B, Ca, Mg, K, Na and Zn were all found to be within the South African limit for agricultural water use (Table 4.25). However, Zn was too high for aquatic ecosystems (<0.002 ppm) (DWAF, 1996). Na was found to be quite high in both sampling seasons, but was still with the limits of 100mg/l limit for what (DWAF, 1996; Fatoki *et al.*, 2002). In a study by Mzini and Winter (2015), they found high concentration Na^+ and Cl^- ions in grey water. This could explain the increase of Na in this study since the river runs through informal settlements where grey water is poured on the ground and finds way to the river. And again, while these concentrations are lower than the maximum permissible limit, Na at about 14 ppm means that for every 1000 litres of water used for irrigation, 14 g of sodium are added into the soil and over the years will results in poor soil structure (Aza-Gnandji *et al.*, 2013). Al-Bassam and Al-Rumikhani (2003) offers an example where 100 mm depth of irrigation containing 1000 ppm of salt if applied to a hectare of soil will effectively deposit 1 ton of salt to that soil.

Fe was found to be above the limits for irrigation water on site 1 and 4 during the dry season, and site 1 and 6 during the wet season. Mn was found to be above irrigation limits on all sites for both seasons except site 2 only. This is very important since the physico-chemical properties show the water to be suitable for irrigation. This implies that a large quantity of water is not suitable to be used in the reduction of poverty and increase food security. Water plays an important role in agriculture for the profitable and sustainable crop production (van der Laan *et al*., 2011). People living near rivers, can use water to irrigate their crops. These crops would ensure access to nutritious food. However, polluted water can not be used for irrigating crops, if it was used, people would be exposed to toxic chemicals from water. Crops contaminated with toxic chemicals would not ensure food security. Food security is defined by the South African National Policy on Food and Nutrition Security (2013) as access to and control over the physical, social and economic means to ensure sufficient, safe and nutritious food at all times, for all South Africans, in order to meet the dietary requirements for a healthy life.

Table 4.25: South African Target water quality Range for livestock watering, crops irrigation and for aquatic use (DWAF 1996, vol 8)

	mg/l		
elements	Livestock watering	Irrigation	Aquatic use
Al	0-5	0-5	40.03
B	0-5	0-5	N/A
Ca	0-1000	N/A	N/A
Fe	0-10	0-5	0.01
Mg	0-500	N/A	N/A
Mn	0-10	0-0.02	0.1
K	N/A	N/A	N/A
Na	0-2000	70	N/A
Zn	0-20	0-1	0.03

Table 4.26: Correlation of metals in water samples for dry season

	Al	*B*	*Ca*	*Fe*	*K*	*Mg*	*Mn*	*Na*
Al	1.000							
B	-0.034	1.000						
Ca	0.143	-0.299	1.000					
Fe	0.809	0.101	0.257	1.000				
K	-0.128	-0.099	0.733	0.176	1.000			
Mg	0.334	-0.292	0.957	0.392	0.550	1.000		
Mn	0.453	0.005	0.461	0.703	0.603	0.486	1.000	
Na	-0.112	-0.160	0.859	0.081	0.947	0.695	0.491	1.000

There was a high correlation for Fe and Al, K and Ca, Mg and Ca, Mg and K, Mn and Fe, Mn and K, Na and Ca, Na and K and Na and Mg (table 4.26).

Table 4.27: correlation of metals in water for wet season

	B	*Ca*	*Fe*	*K*	*Mg*	*Mn*	*Na*	*Zn*
B	1.000							
Ca	0.152	1.000						
Fe	0.629	0.552	1.000					
K	-0.185	0.685	-0.048	1.000				
Mg	0.200	0.946	0.609	0.551	1.000			
Mn	0.314	0.740	0.706	0.519	0.719	1.000		
Na	0.001	0.919	0.329	0.892	0.805	0.707	1.000	
Zn	0.146	0.275	0.290	-0.131	0.227	0.222	0.064	1.000

For wet season, there was a very strong correlation between most of metals. Zn was the only metal with no strong correlation (table 4.27). The good correlation shows that the metals originated from the same source (Okedeyi, 2012)

Table 4.28: Water physico-chemical properties for dry season

	EC (mS/m)	pH	Tot. Alkalinity (ppm)	Cl (ppm)	TDS (ppm)
site 1	15.76	7.29	40.00	14.20	96.14
site 2	22.00	7.19	50.04	7.10	134.20
site 3	30.37	7.10	68.11	28.40	185.26
site 4	20.33	7.25	45.08	21.30	124.01
site 5	19.28	7.23	45.08	21.30	117.61
site 6	30.51	7.17	60.10	24.85	186.11

Table 4.29: Water physico-chemical properties for wet season

	EC (mS/m)	pH	Tot. Alkalinity (ppm)	Cl (me/L)	TDS (ppm)
site 1	16.76	7.31	35.06	28.40	102.24
site 2	22.10	7.04	55.09	28.40	134.81
site 3	22.54	7.04	55.09	31.95	137.49
site 4	22.53	7.06	60.10	28.40	137.43
site 5	21.81	7.14	60.10	28.40	133.04
site 6	27.71	7.08	75.13	28.40	169.03

Table 4.28, presents some of the physico-chemical properties for the dry season sampling. The EC ranges from 15.76 to 30.51 mS/m. the highest is site 6, with a corresponding high TDS of 186.11 ppm. The lowest TDS is observed in site 1 at 96.14

ppm. The TDS increases from site 1, site 2, site 3 then site 6. Site 4 and 5 are not in this trend, this may be due to the fact that these sites are separated from the other sites. The pH range was between 7.17 and 7.29. pH is important in the mobility of metals, with low pH favouring mobility. The chlorides range was between 14.20 and 28.4 ppm.

Table 4.29, present physico-chemical properties for the wet season. The EC range was between 16.76 to 27.71 mS/m. the low EC was found on site 1 while the high value occurred on site 6 the highest. The same is true for TDS at 102.4 and 169.03 ppm. The chlorides were all at 28.4 ppm except for site 3 which was 31.95. The pH range was between 7.06 and 7.31. The EC ranges for both sampling seasons were well within the limits (0-40 mS/m) for good water for irrigation (van der Laan *et al.*, 2011). The pH also falls in the range of good water (van der Laan *et al.*, 2011).

The chlorides are important nutrients for plants but can be toxic at high concentration (Aza-Gnandji *et al.*, 2013). The maximum allowed chlorides for irrigation water is 100 ppm (DWAF, 1996). All the chloride values were well below the maximum.

4.6 Pops in sediments

4.6.1 Method development

A commercial mixture of organochlorine pesticides (OCP) was injected on the GC/MS for analysis. This was done in order to be used as tool of identifying unknowns. The accompanying chromatogram is shown on figure 4.7. Table 4.30 lists the identified OCPs, their retention times, as well as method detection limits.

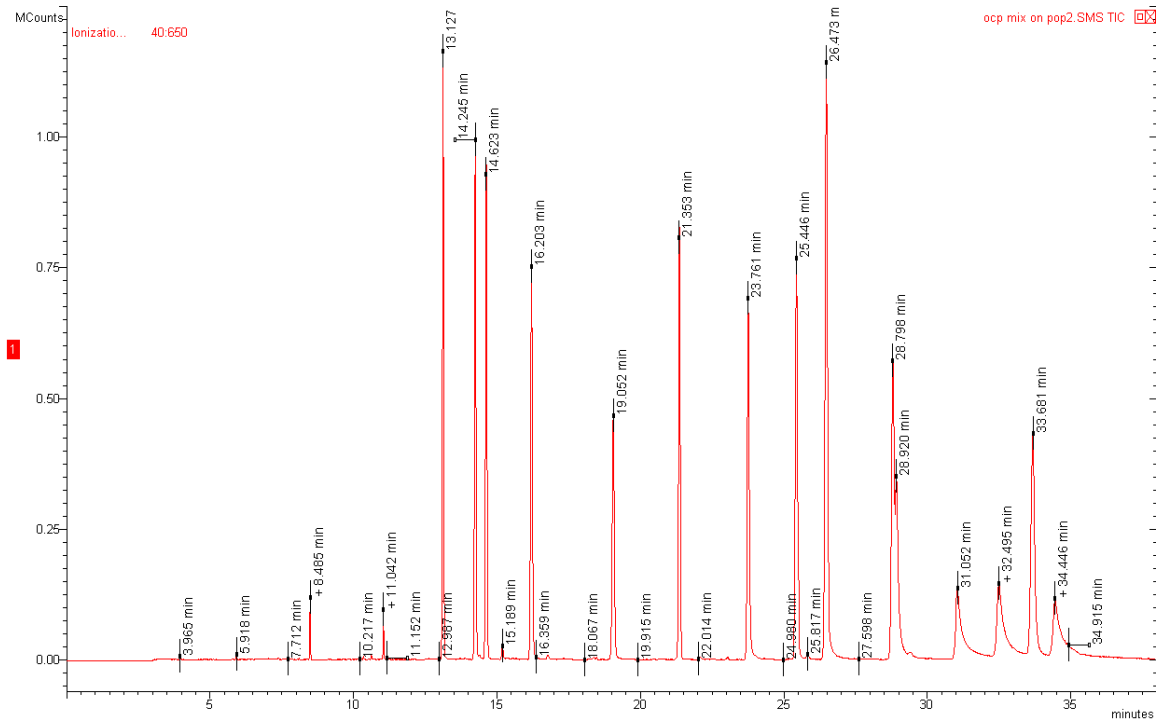

Figure 4.7: Chromatogram of a commercial organochlorine pesticides.

Table 4.30: Identified components in the OCP mixture

Name of OCP	Retention time	Kovat retention index	LoD (ppm)
Alpha-BHC	13.129	1717	1.255
Gamma-BHC(lindane)	14.248	1762	0.467
Beta-BHC	14.629	1778	0.674
Delta-BHC	16.194	1830	1.019
heptachlor	19.039	1912	0.540
Aldrin	21.358	1980	0.625
Heptachlorepoxide	23.758	2168	0.451
Gamma-chlordane	25.451	2323	0.534
Alpha-chlordane	26.478	2399	0.554
Dieldrin/4,4`DDE	28.923	2551	0.542
4,4'-DDD	33.681	2753	0.404

Commercial PCBs were purchased and injected on the GC/MS to be analysed in order to be used for identification of unknowns; these are shown in figure 4.8 to figure 4.11.

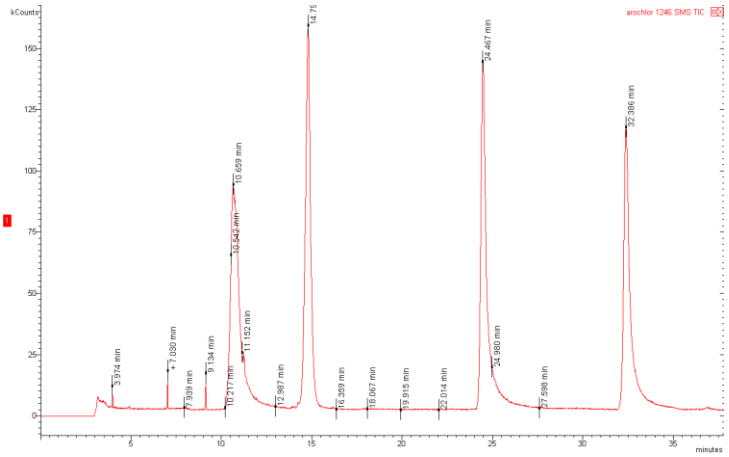

Figure 4.8: Chromatogram of Aroclor 1248

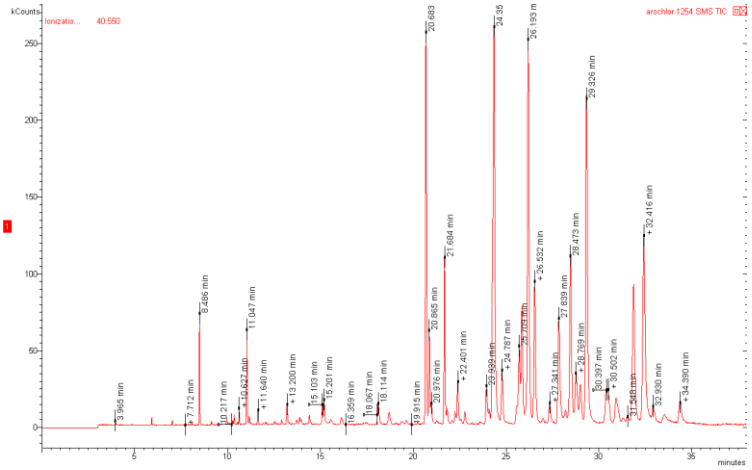

Figure 4.9: Chromatogram of Aroclor 1254

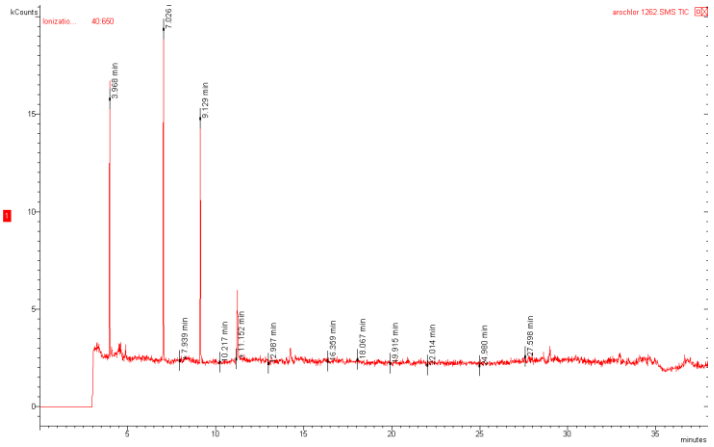

Figure 4.10: Chromatogram of Aroclor1262

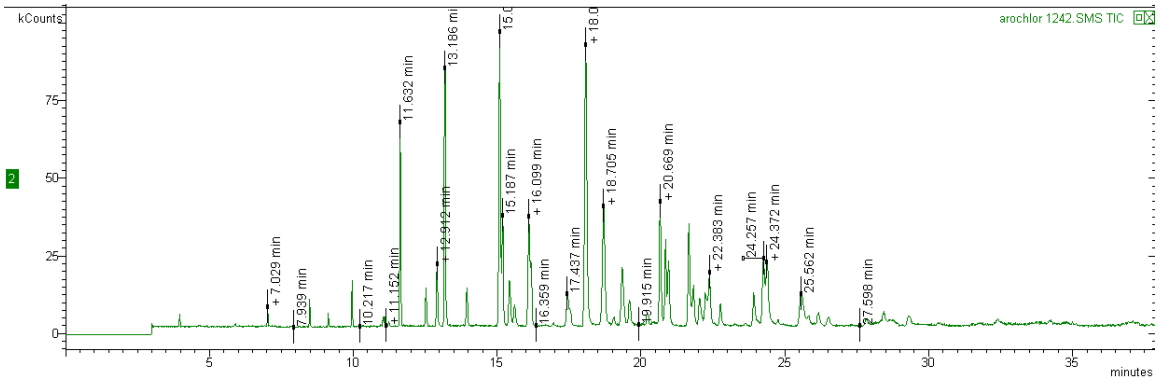

Figure 4.11: Chromatogram of Aroclor 1242

Table 4.31: Table of identified compounds on the PCB mixtures

Compound name	Retention time	Kovat retention index (from NIST)
2,2,4'-trichorobiphenyl	18.087	1884
2,2',5-trichorobiphenyl	15.081	1779
1,1'-Biphenyl,2,3,3'-trichloro	16.179	1827
Biphenyl,3,3'-dichloro	13.178	1714
endrineketone	24.477	2237
p,p'-DDT	14.826	1786
Methoxychlor olefin	32.374	2651

4.6.2 Determination of Kovat retention Index

In order to facilitate the identification of unknown on the chromatograms, Kovats retention indices were used, and these are shown in table 4.31. Identification of unknown on the GC/MS analysis can be done by analysing known compounds and match retention times. If known compounds are not available, the search library on the mass spectrometry can be used. The challenge of using the electronic libraries is that sometimes more possible compounds are given by the search making identifying to be difficult (Goodner, 2008). The Kovats retention index reflects the retention behaviour of compound in relatively to the standard set of hydrocarbons immediately before and after the compound (Jalali-Heravi and Fatem, 2001). For this study a mixture of alkanes was injected in the column and eluted using a method used for analysis of unknowns (figure 12a and 12b). Equation 4.1 was then used to calculate the indices.

$I_x = 100n + 100(t_x-t_n) / (t_{n+1} - t_n)$ equation 4.1 [http://webbook.nist.gov/chemistry/gc-ri/ accessed on 22/01/2016]

Where:

I_x = Kovats retention index of the unknown

n = the number of carbon atoms in the smaller n-alkane

n+1 = the number of carbon atoms in the larger n-alkane

t = retention time

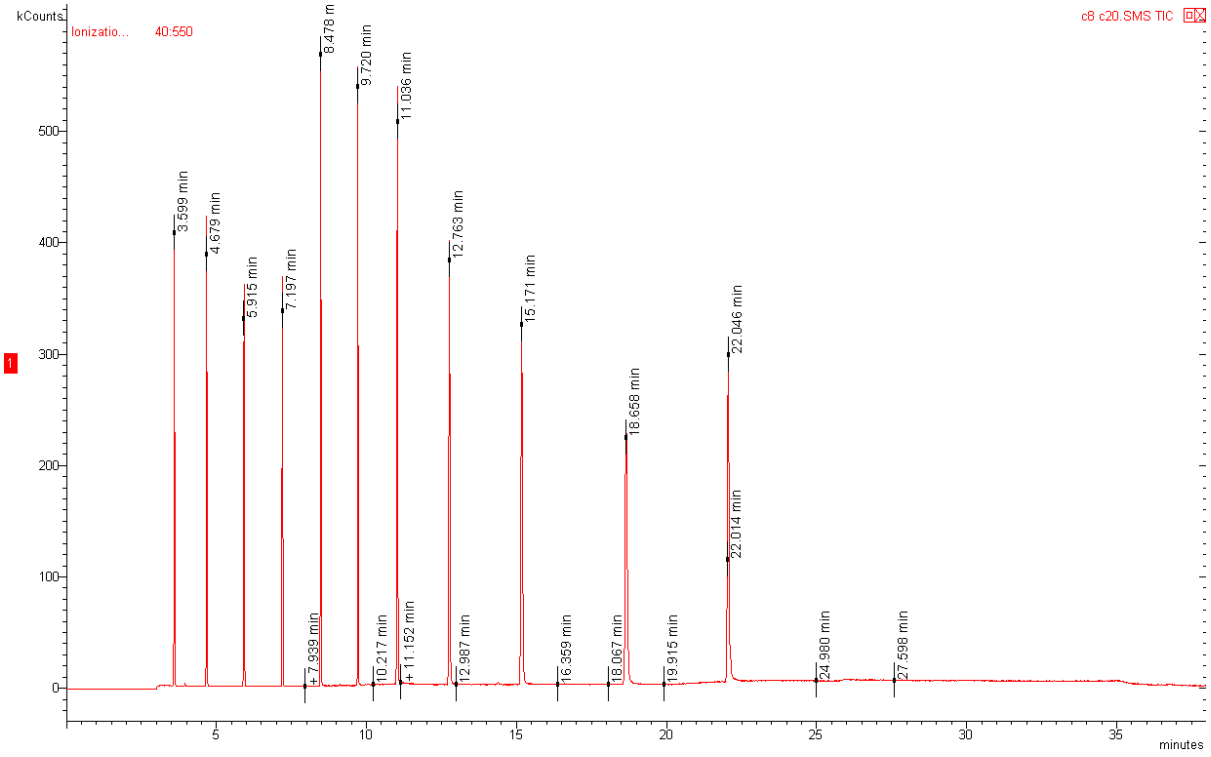

Figure 4.12a: Chromatogram mixture of alkanes C_{10}-C_{20}

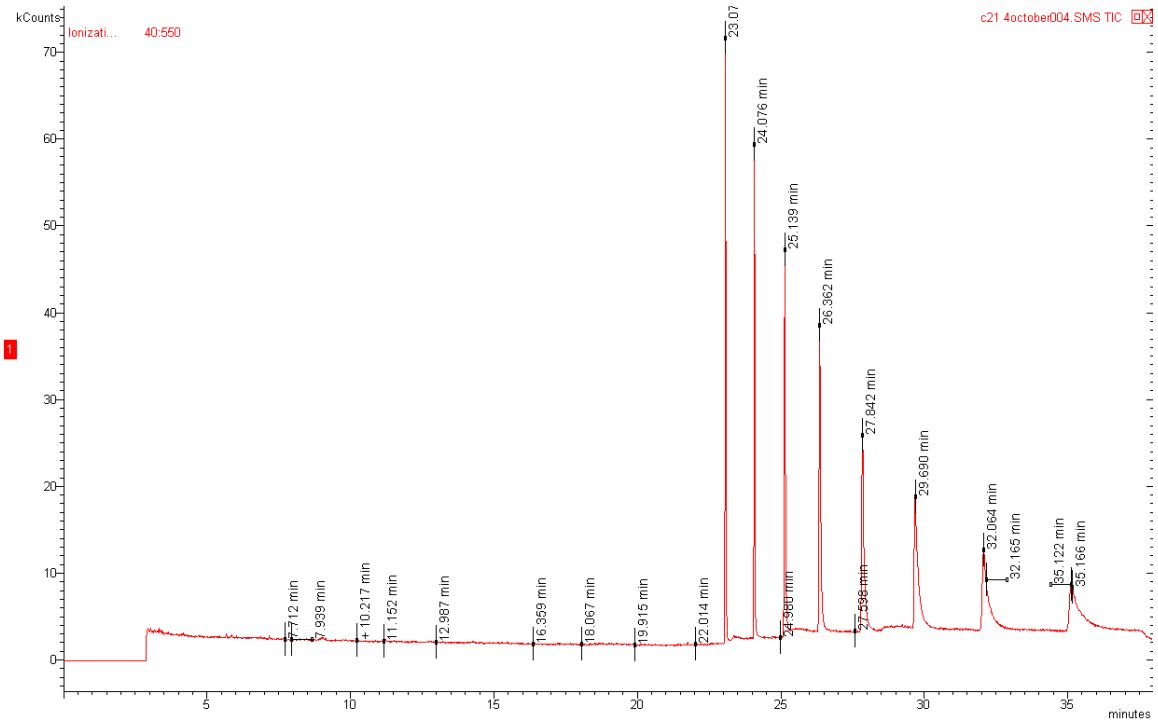

Figure 4.12b: chromatogram mixture of alkanes C_{21}-C_{28}

4.6.3 Analysis of POPs extractions from site 1 to site 6

The extraction obtained from sites 1 to 6 were then analysed on the GC/MS using the developed method. However, none of the identified POPs were detected on the analysis of sampled sites. It is possible that the compounds were present but in low concentration and could not be detected by the low resolution GC/MS. In fact, the chromatograms obtained during analysis were mostly solvent peaks. Prepared calibration standards were diluted to down to produce 0.001, 0.008, 0.016 and 0.01 ppm but there was no detection. A determined detection limit of our method was about 0.4 ppm. Environmental pollutants can be present in much lower concentration. In such cases, the use of indicator organisms which concentrate the pollutants is the only viable way (Carneiro *et al*., 2015). However, instruments with improved sensitivity such as a high resolution mass spectrometry and Liquid Chromatography mass spectroscopy are recommended (Krska *et al.*, 2012). This statement can be supported by the fact that sediments spiked with POPs and OCPs were analysed positively by the GC/MS. This could be because the spike concentrations were higher than those present in environmental samples. Muhammad *et al.*, (2016), concur that the normal GC/MS cannot be used solely as a monitor of environmental pollutants due to low

sensitivity and an inability to resolve some chemical pollutants. When peaks are co-eluting, contaminants cannot be identified or quantified (Lozowicka *et al*., 2012).

CHAPTER FIVE: CONCLUSION AND RECOMMENDATIONS

This chapter presents the conclusion and recommendations based on the research findings.

5.1 Introduction:

The major aims of this study were to determine trace metals and POPs in the Baynespruit River, Sobantu, KwaZulu-Natal. This was achieved by collecting samples from the river for dry and wet season. Samples included sediments, water and plants. Selected and verified methods of extraction and analysis were applied on the samples. Analysis was carried out on the ICP-OES, AAS and GC/MS.

5.2 Summary.

In this study, the sediments were found to have high concentrations of Cu, Cr, Pb and Zn. The concentration order for both sampling seasons was Zn > Cu > Cr > Pb. In terms of dry and wet the season, Zn was 96.37 and 132.5 mg/kg, Cu was 27.59 and 130.7 mg/kg, Cr was 63.51 and 75.36 mg/kg, Pb was 33.40 and 41.91 mg/kg respectively. In a similar study by Mullan *et al.*, (2015), the following values were found for metals in dry and wet season respectively; Zn was 72.71 and 99.20 mg/kg, Pb was 19.24 and 22.21 mg/kg, Cu was 14.53 and 22.68 mg/kg, Cr was 30.13 and 37.52 mg/kg. The rain during the wet season seemed to play a role that increased the concentration of metals. The order of concentration of metals is also similar, except for Cr and Cu which changes position. In the current study, there is more Cu than Cr. The high levels of these metals suggest they arise from anthropogenic activities such as high traffic density and industrial activities (Singo, 2013).

Lead sources from manmade activities include pesticides (Mcbride, 2013). Lead toxic levels affects enzyme activity resulting in inhibited germination, reduced rate of photosynthesis, transpiration, gaseous exchange and chlorophyll formation (Khan *et al.*, 2013).

Results of the study of the bio-available metals showed that the metals mobilised on the river sediments does became available to the plants at later stages. The average of concentration values of all sites for K, Ca, Mg, Zn, Mn and Cu were 75.05, 1474.22, 281.39, 19.86, 33.55 and 9.09 mg/kg for the dry season respectively. For the rainy seasons, concentration values were 95.28, 1368.17, 314.22, 28.62, 114.61 and 36.31

mg/kg respectively. Metals such as Cu, Mn were found to be above the WHO limits for edible plants. Further comparison with similar studies in South Africa suggest that these metals originate from anthropogenic activities. These results are very much comparable with results obtained from waste dumping sites than those of natural systems (Lion and Olowoyo, 2013). The bio-available portion of metals in the environment is the one that poses immediate threats to the biosphere.

The sediments total metals and bio-available metals confirmed that sediments act as sinks of pollutants in the aquatic systems. While other metals such as Ca, Mg and K are regarded as good metals even in agriculture, they still need to be monitored in the environment. This is because metal toxicity or deficiency does not arise just because of the presence or the absence thereof, but on all factors including interaction amongst metals (Herselman, 2007). For example, excess Na in soil can affect the uptake of Ca and Mg by plants (Al-Bassam and Al-Rumikhani, 2003; van der Laan *et al.*, 2011).

The pH of the sediments was found at region of slightly acidic 5.12 to 7.61; however, most sites were between the pH 5-6. Low pH favours the incorporation of metals into the solution. Higher pH precipitates metals out of solution. Metals in solution are the ones that become available to plants by absorption. However, precipitated or bound metals can still be ingested by living organisms. Al is known to be toxic to plants at low pH. It can be controlled by liming which increases the pH (Singo, 2013). This implies that applying irrigation water with aluminium can be costly in the future when rehabilitation is required.

Results of plant analysis showed that the plants growing on the river edge are highly contaminated with metals. This applies to both edible and non-edible plants. Some of the metal concentration exceeded the WHO maximum limits. Vegetables including those that grow on their own are important to some South African communities since they are used as source of nutrients as well as herbal medicines (Olowoyo *et al.*, 2012). However, the results presented here highlight a threat that can be posed by such vegetables if their pollution status is not tested. They can effectively become a medium of transfer of toxic metals from industries direct to the people. Plants are good concentrators of environmental pollution. Toxic substances occurring in small amounts can be found in high concentration in plant parts. This is because these toxic

compounds are not degradable and they can increase up the food chain by bio-magnification (Pellacani *et al*., 2012; Kang *et al*., 2013).

The physico-chemical properties of water were found to be within the acceptable limits in terms of pH, EC, TDS, Cl an alkalinity for agricultural purposes. This was true for both sampling seasons. The average values for dry season were as follows pH 7.21, EC 23.04 mS/m, total alkalinity ($CaCO_3$) 51.40 ppm, chlorides 22.01 ppm and TDS 140.56 ppm. For the wet season the values were pH 7.11, EC 22.24 mS/m, total alkalinity ($CaCO_3$) 56.76 ppm, chlorides 29.11 ppm, TDS 135.67 ppm.

The results of metals for the water column were low and most elements were within the limits of agricultural water use. However, it is worth noting that for irrigation water analysis, the factors usually considered are pH, Cl, TDS, Alkalinity, and SAR. The SAR requires Ca, Mg and Na cations to be known before calculation. As stated before, the water under study passed this test however Mn is above the limits for irrigation water (DWAF, 1996). On all sites and on both seasons Mn was high except on site 2. This implies that, since there are guidelines for irrigation water, testing must use these guidelines and cover all parameters.

POPs were not detected from the sediments, however more work needs to be done and analysis be conducted on instruments with high sensitivity before conclusions could be drawn on the occurrence of the POPs in the sediments.

5.3 Conclusions:

This study has achieved the objectives of determining metal pollutants in the Baynespruit River, Sobantu, KwaZulu-Natal. Also, a method for the determination of POPs was developed and validated successfully. However no POPs were found during this work. The overall results show that this river is polluted with metals. While some of these metals are required by some living organisms, some such as lead are not needed at all but was found to be present. The availability of these metals to the biota poses a threat to the ecosystems and humans.

The levels of these metals which were found to be above suggested background levels suggest that these metals arise from anthropogenic activities. The study also showed that there is a link on metals in the river, sediments and biota. Though metals can be

present in low amounts in the water column, they become concentrated in sediments and the biota.

While the water was found to be suitable for irrigation, prolonged use of contaminated water will result in the increase of contamination on the receiving soil and crops. For example, Mn and Zn were found in the water column, transfer of this water will carry these to fields, and overtime the concentration will increase in the soil.

High levels of metals found in the plants growing on the river bank should not be used by the people for consumption or for medicinal purposes. Animals feeding and drinking on the river will also be exposed to trace metal contamination.

If the issue of pollution in this river is not addressed, more metals will contaminate the water and surrounding environmental compartments. It is up to the responsible authorities to control and monitor the pollution of aquatic systems.

5.4 Recommendations.

Based on the results of this study, it is recommended that:

- Further monitoring of this river for trace metals be carried out in order to establish the long term trend.
- More samples per sampling area are required so that the standard deviation will be low and results will be more meaningful.
- Baseline pollution of rivers needs to be established, and municipalities to monitor any further changes. Simple stating of maximum allowed limits for pollutants does not help much since overtime they increase above this and requires expensive remedial actions.
- More meaning on the maximum limits of metals in the water columns need to be added, since the areas affected are the ones receiving the water column.
- POPs studies must be carried out using advanced extraction methods and high resolution mass spectroscopy.
- Heavy metal testing on irrigation water from rivers must be mandatory for all service providers.
- Children of the communities around this river should be prevented from using this water to play with.

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Appendices

Appendix 1: ethics clearance

UNISA university of south africa

CAES RESEARCH ETHICS REVIEW COMMITTEE

Date: 25/11/2014

Ref #: **2014/CAES/150**
Name of applicant: **Mr VT Zuma**
Student #: **40952967**

Dear Mr Zuma,

Decision: Ethics Approval

Proposal: Determination and characterization of trace metals and persistent organic pollutants in Baynespruit River, Sobantu, Kwazulu-Natal

Supervisor: Mr N Baloyi

Qualification: Postgraduate degree

Thank you for the application for research ethics clearance by the CAES Research Ethics Review Committee for the above mentioned research. Final approval is granted for the duration of the project.

The application was reviewed in compliance with the Unisa Policy on Research Ethics by the CAES Research Ethics Review Committee on 25 November 2014.

The proposed research may now commence with the proviso that:

1) *The researcher/s will ensure that the research project adheres to the values and principles expressed in the UNISA Policy on Research Ethics.*
2) *Any adverse circumstance arising in the undertaking of the research project that is relevant to the ethicality of the study, as well as changes in the methodology, should be communicated in writing to the CAES Research Ethics Review Committee. An amended application could be requested if there are substantial changes from the existing proposal, especially if those changes affect any of the study-related risks for the research participants.*
3) *The researcher will ensure that the research project adheres to any applicable national legislation, professional codes of conduct, institutional guidelines and*

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scientific standards relevant to the specific field of study.

Note:
The reference number [top right corner of this communiqué] should be clearly indicated on all forms of communication [e.g. Webmail, E-mail messages, letters] with the intended research participants, as well as with the CAES RERC.

Kind regards,

Signature
CAES RERC Chair: Prof EL Kempen

Signature
CAES Executive Dean: Prof MJ Linington

PLEASE NOTE CONDITIONS

Appendix 2: Municipal permission

The Msunduzi Municipality

Private Bag X 321
Pietermaritzburg
3200
Φ (033) 392 3000

333 Church Street
Pietermaritzburg
3200
www.msunduzi.gov.za

CITY OF CHOICE
PIETERMARITZBURG
MSUNDUZI

Enq:MR SINGH | Tel: 033-3922343 | E-mail: vishal.singh@msunduzi.gov.za

14 July 2014

To whom it may concern
University of South Africa

Dear Sir/ Madam

This serves to confirm that Mr V Zuma (student no. 40952967) will be conducting water sampling along the Baynespruit for the duration of his masters programme.

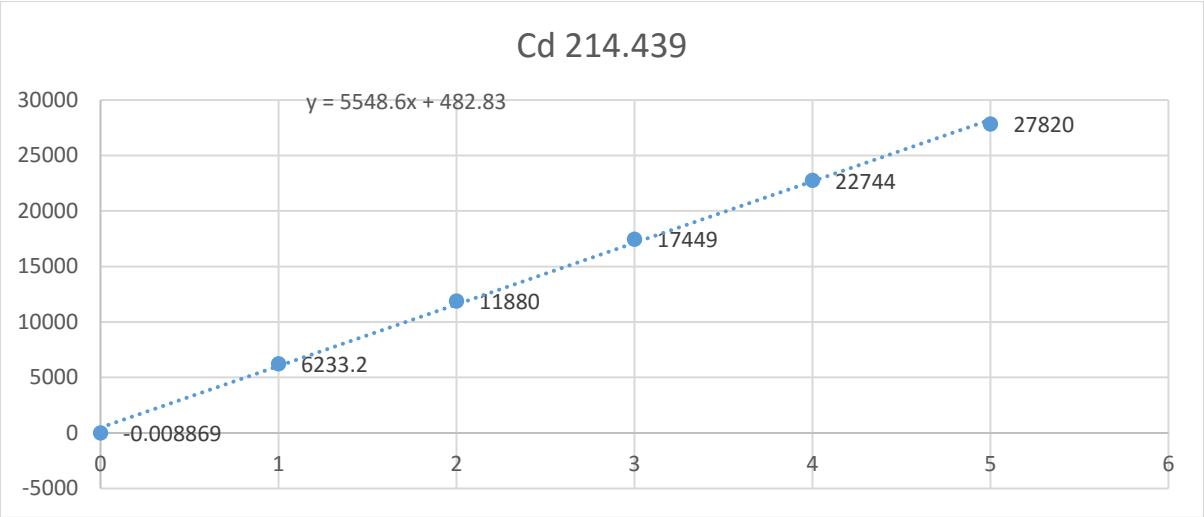
ENVIRONMENTAL HEALTH MANAGER

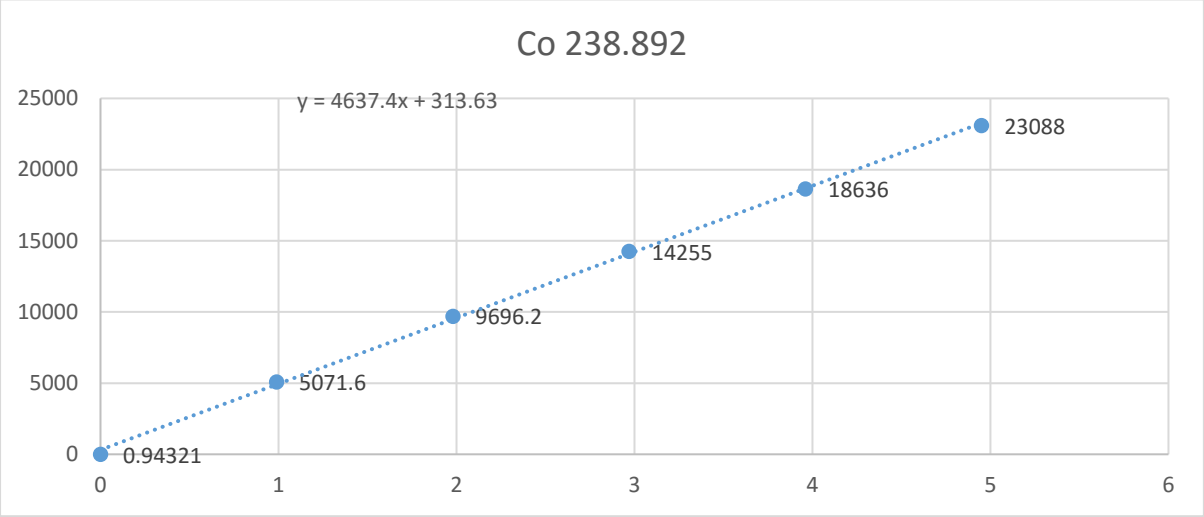
COMMUNITY SERVICES

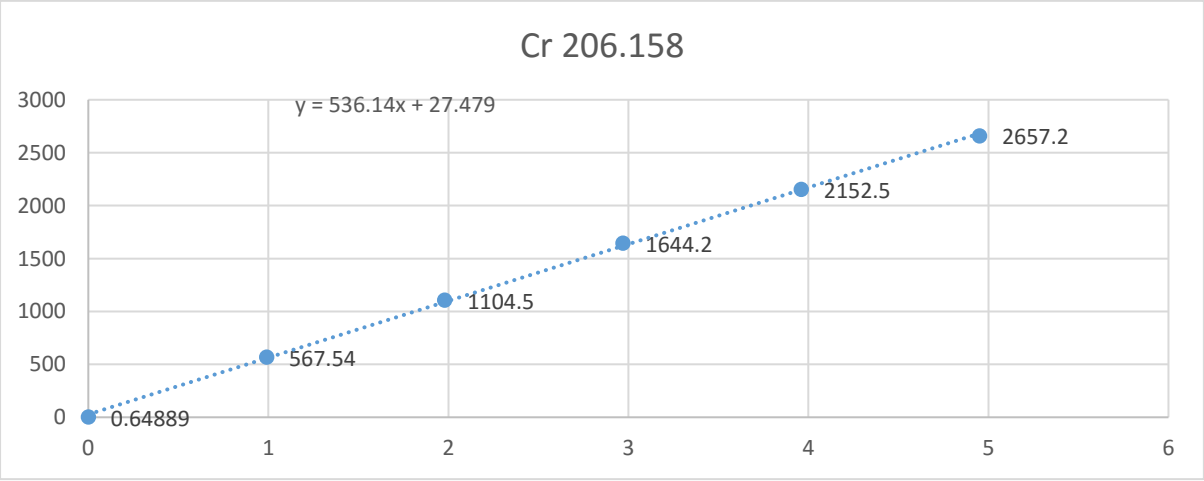
Telephone/uCingo: 033 3922880
Facsimile/ifekisi: 033 3922419

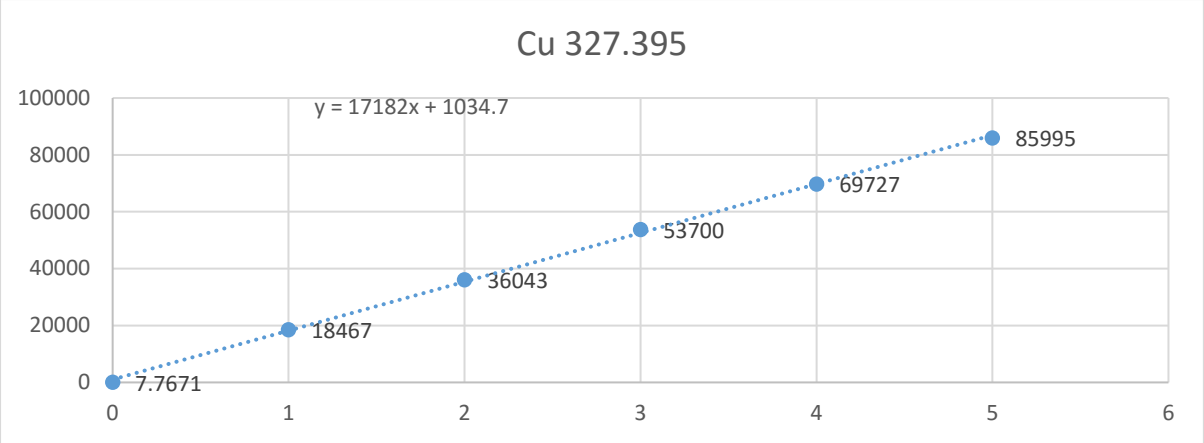
Private Bag / Isikhwama: X 321
Pietermaritzburg/ePietermaritzburg 3201

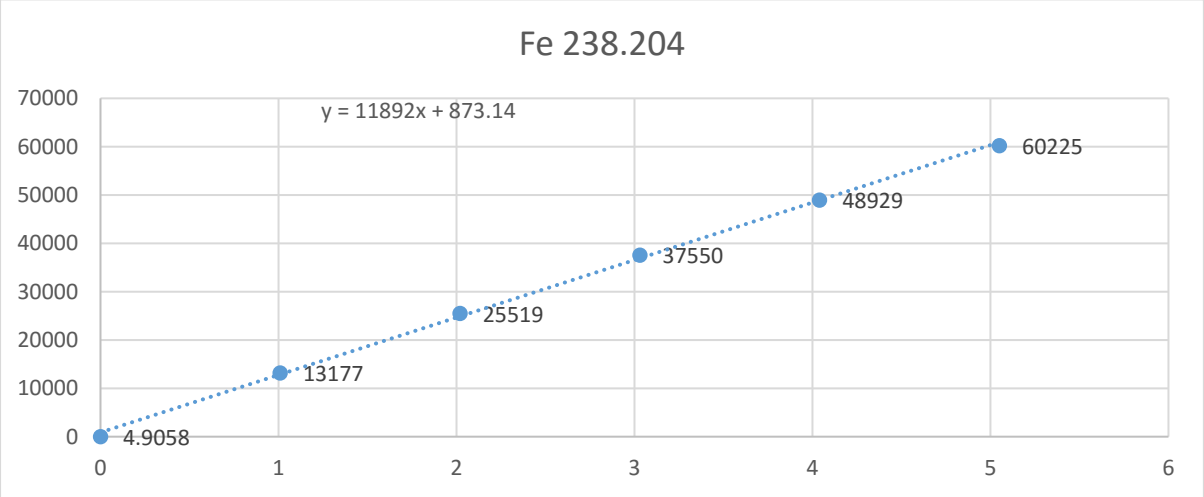
Appendix 3: calibration graphs for determination of LoDs

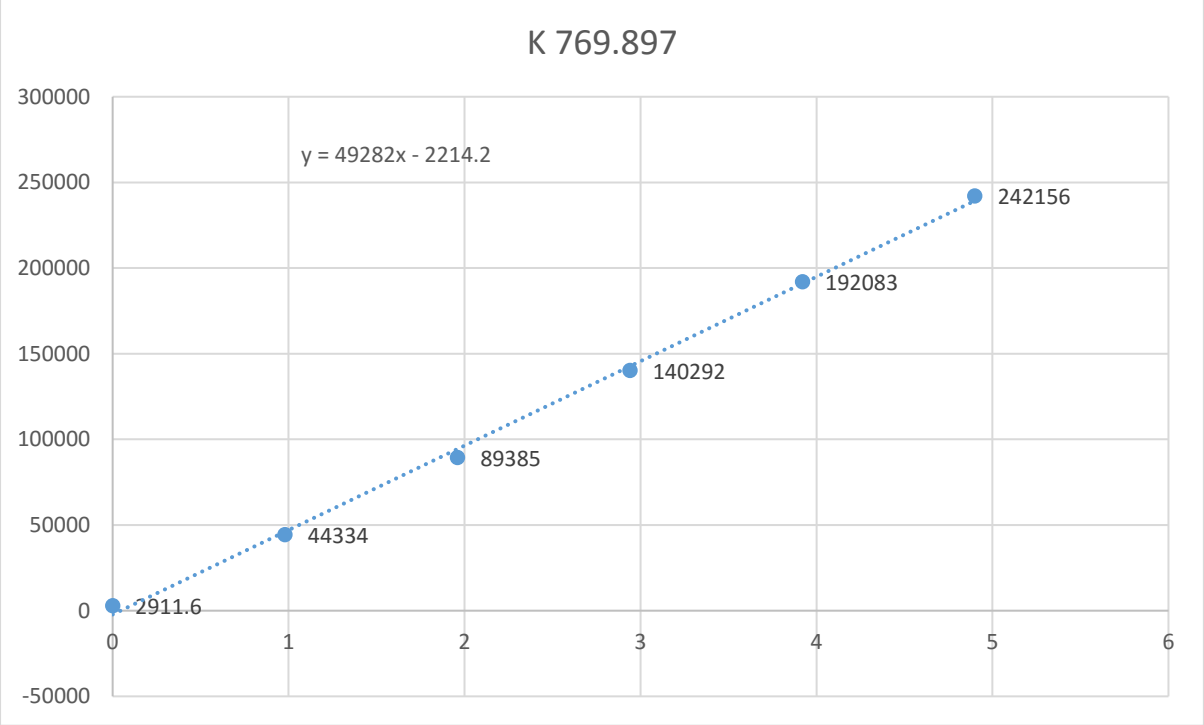


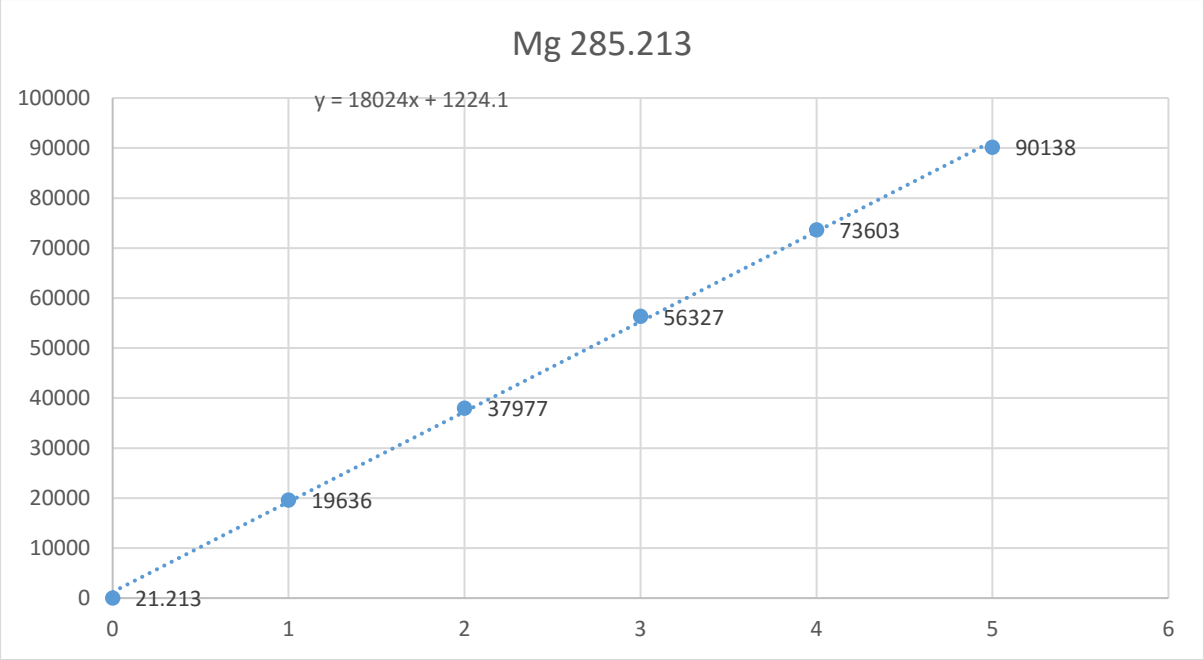


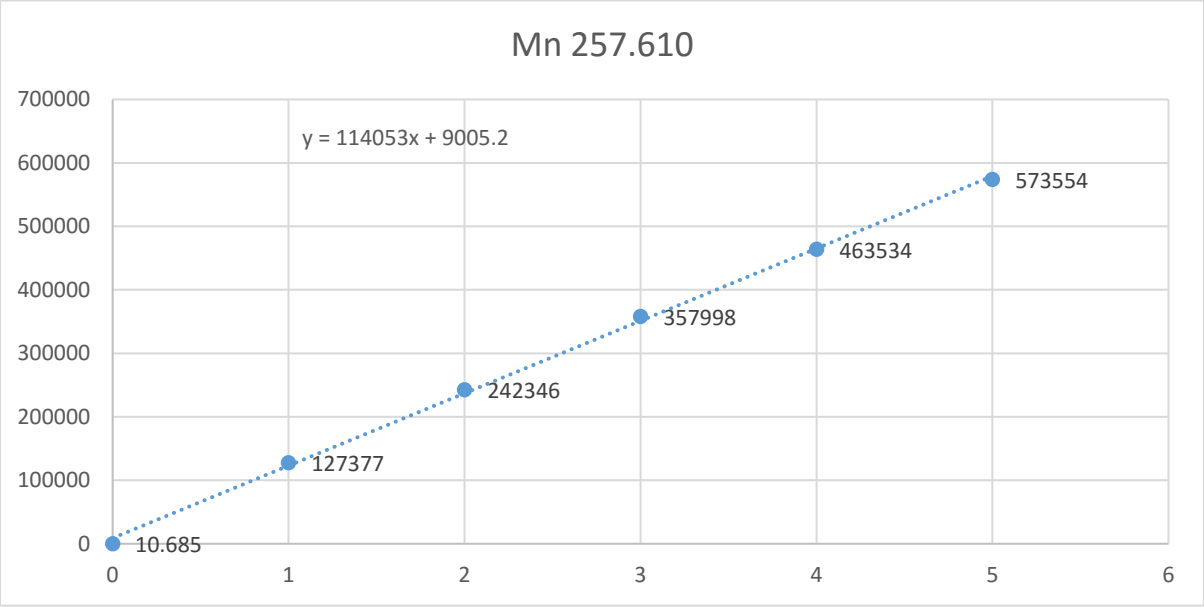


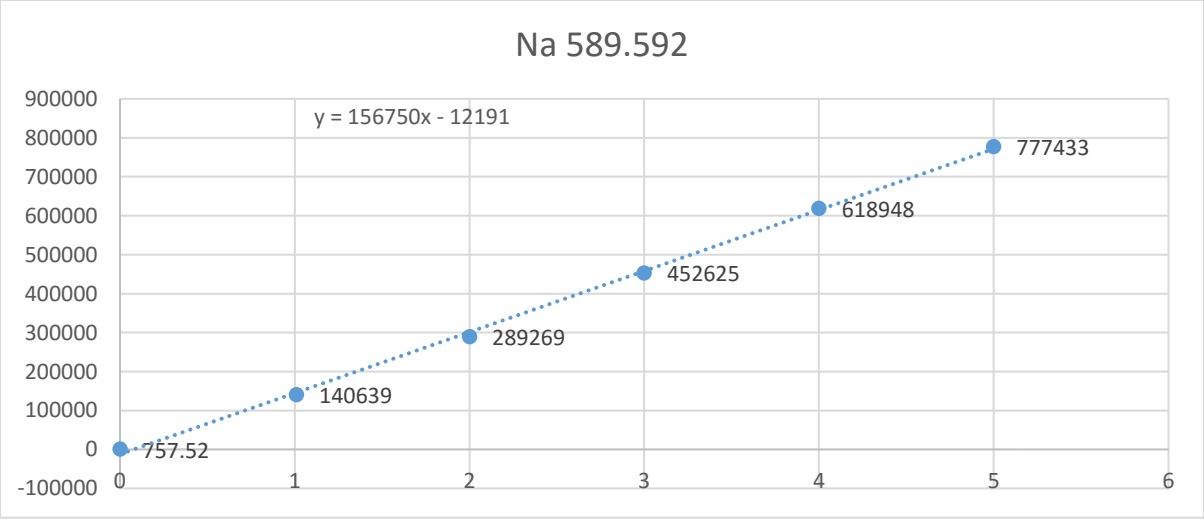

Cu 327.395
y = 17182x + 1034.7
100000
80000
60000
40000
20000
0
0
1
2
3
4
5
6
7.7671
18467
36043
53700
69727
85995

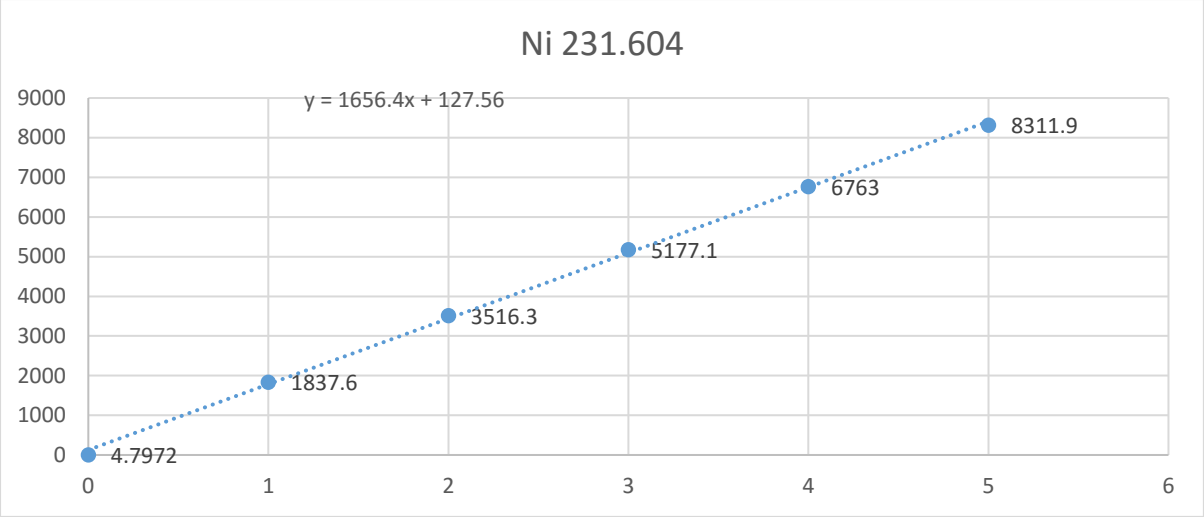

Fe 238.204
y = 11892x + 873.14
70000
60000
50000
40000
30000
20000
10000
0
0
1
2
3
4
5
6
4.9058
13177
25519
37550
48929
60225

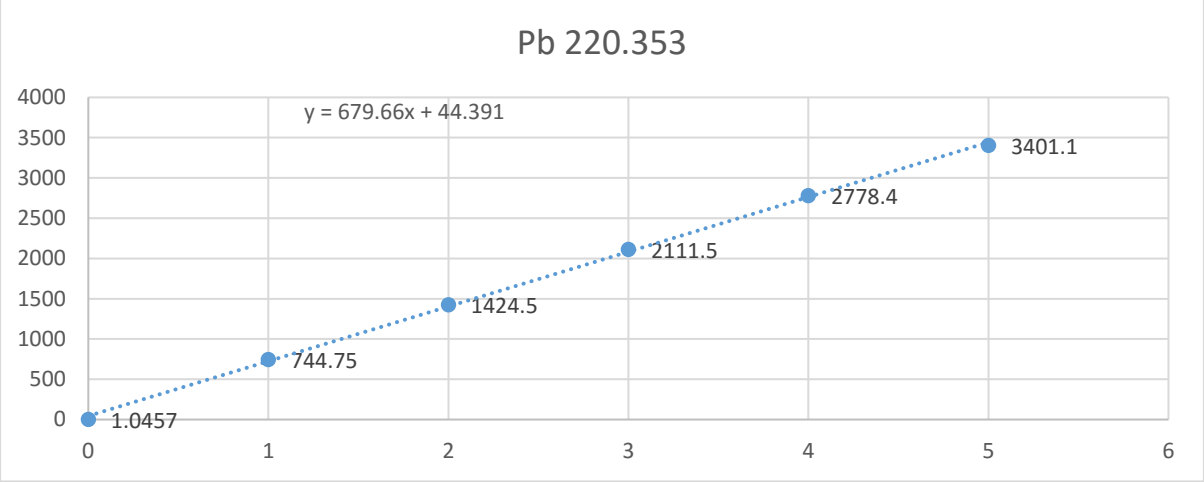

K 769.897
y = 49282x - 2214.2
300000
250000
200000
150000
100000
50000
0
-50000
0
1
2
3
4
5
6
2911.6
44334
89385
140292
192083
242156


Mg 285.213
y = 18024x + 1224.1
100000
90000
80000
70000
60000
50000
40000
30000
20000
10000
0
0
1
2
3
4
5
6
21.213
19636
37977
56327
73603
90138


Mn 257.610
y = 114053x + 9005.2
700000
600000
500000
400000
300000
200000
100000
0
0
1
2
3
4
5
6
10.685
127377
242346
357998
463534
573554


Na 589.592
y = 156750x - 12191
900000
800000
700000
600000
500000
400000
300000
200000
100000
0
-100000
0
1
2
3
4
5
6
757.52
140639
289269
452625
618948
777433


Ni 231.604
y = 1656.4x + 127.56
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
0
1
2
3
4
5
6
4.7972
1837.6
3516.3
5177.1
6763
8311.9


Pb 220.353
y = 679.66x + 44.391
4000
3500
3000
2500
2000
1500
1000
500
0
0
1
2
3
4
5
6
1.0457
744.75
1424.5
2111.5
2778.4
3401.1

Appendix 4

Chromatograms obtained from the analysis of site 1 to site 6 are shown in figure 4.13 to figure 4.18.

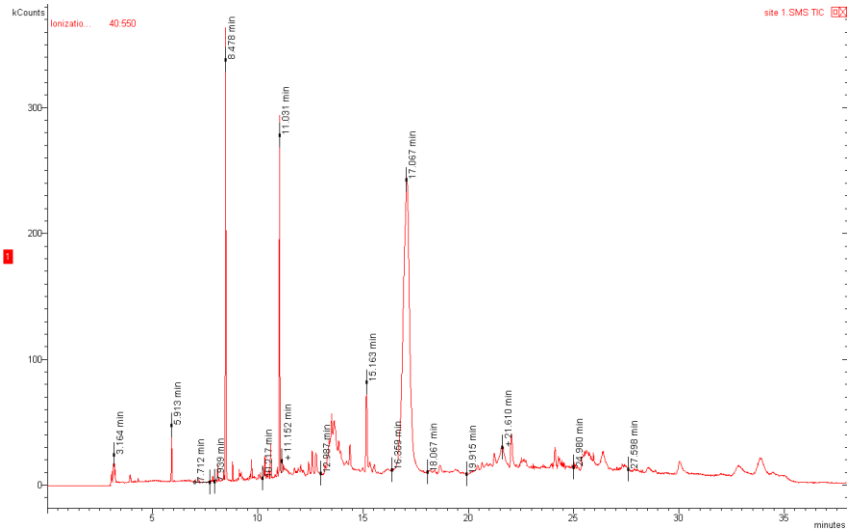


Figure 4.13: Chromatogram of site 1 sediment extract

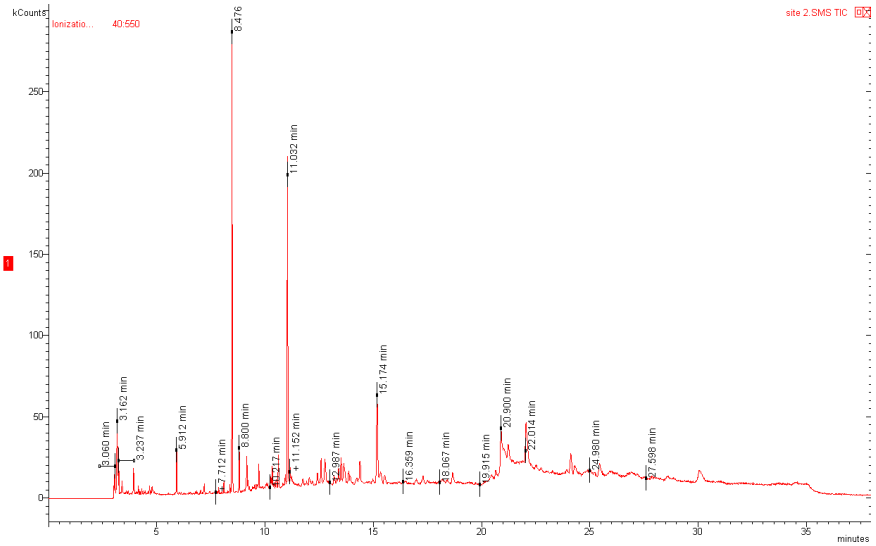


Figure 4.14: Chromatogram of site 2 sediment extract

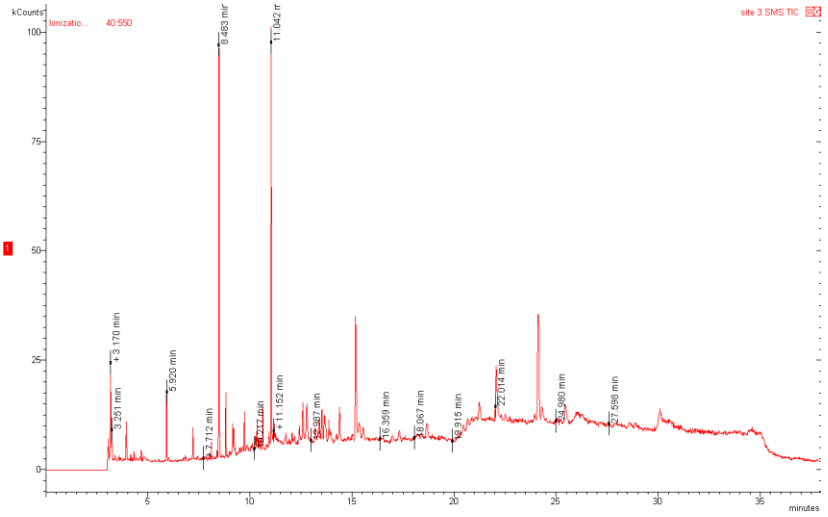


Figure 4.15: Chromatogram of site 3 sediment extract

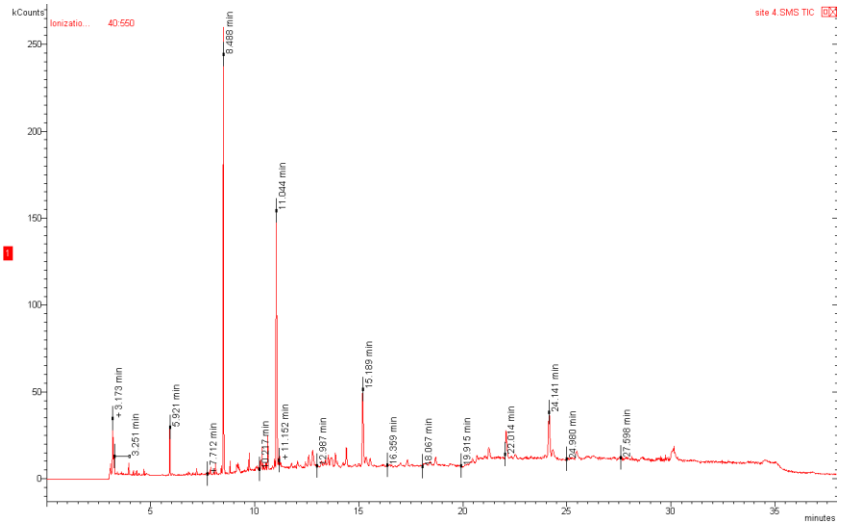


Figure 4.16: Chromatogram of site 4 sediment extract

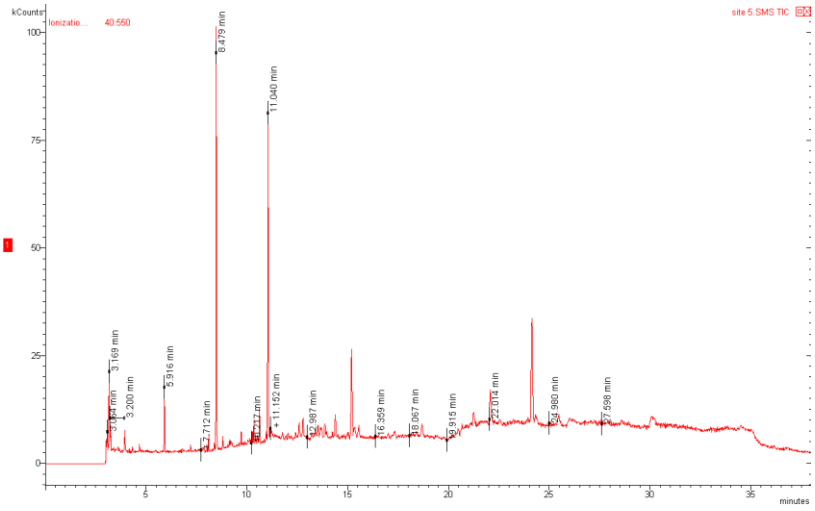


Figure 4.17: Chromatogram of site 5 sediment extract

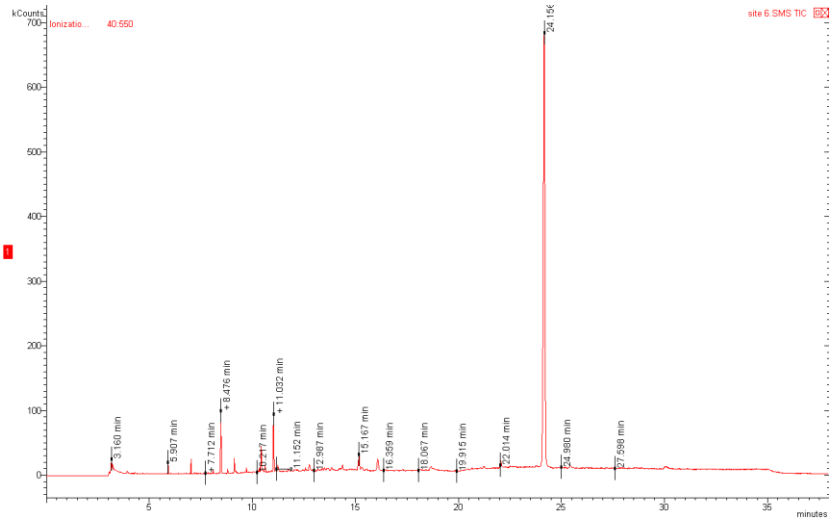


Figure 4.18: Chromatogram of site 6 sediment extract